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Journal of the
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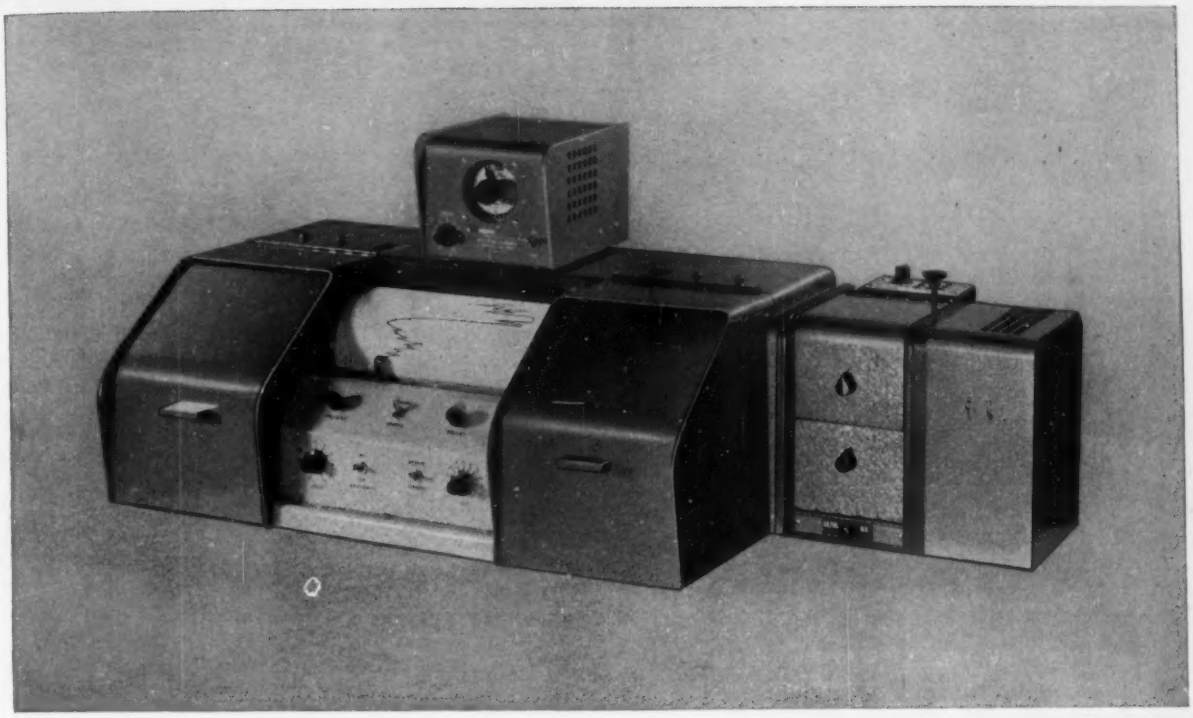

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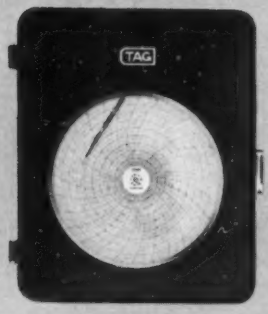

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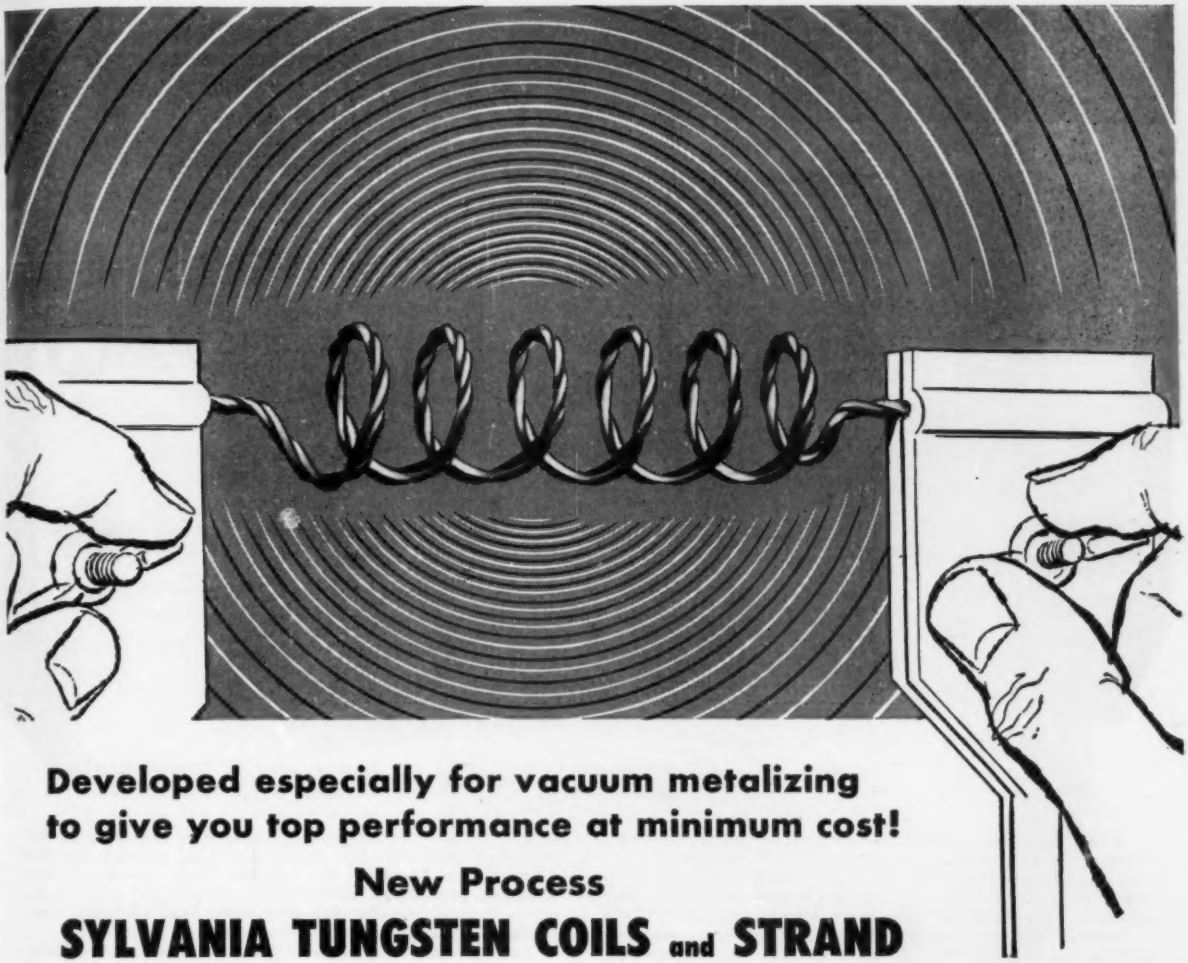

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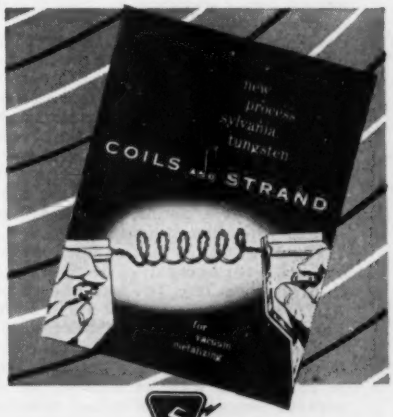

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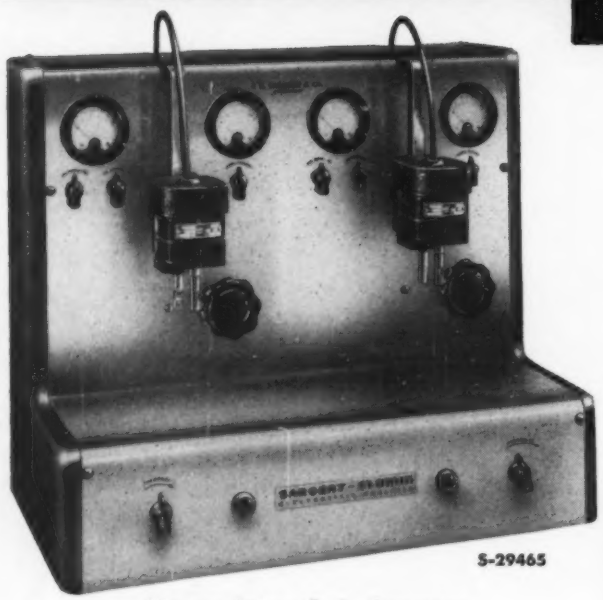

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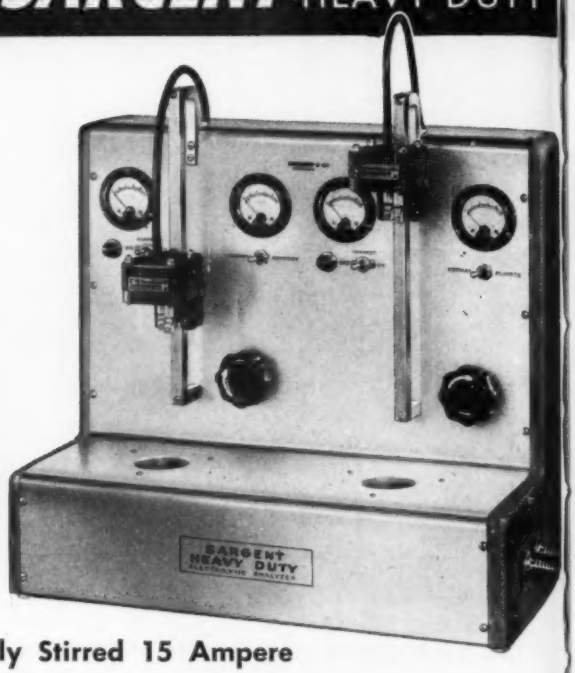

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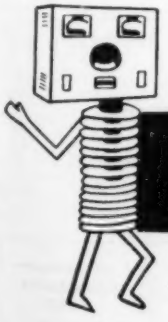

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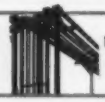
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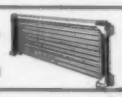
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Editorial

Josiah Willard Gibbs and The Hall of Fame

WHAT IS MEANT by the word "fame"? Dictionaries list as definitions such phrases as *lofty reputation* and synonyms like *renown*, but they don't seem to help much. The trouble is that there are many kinds of fame. It varies from "the bubble reputation," to that which lasts centuries, such as that of Alexander the Great or of Mohammed. A bit fancifully we may think of fame as analogous to potential energy. It may be transformed into other forms quickly or slowly. And, like energy, fame may be considered to have intensive and extensive factors. Thus a person, or historic figure, may be widely known but may engage the interest of the general public very little. On the other hand, a man may have been known to a relatively small number of people during his lifetime and after his death but may have been and remain very important to those few people, and, through this selected and devoted few, may have great influence on the world at large. Thus the fame of Josiah Willard Gibbs may be said to have a high intensity factor and a narrow extensive range.

Gibbs was, certainly, the greatest scientist that America has produced. A recent, and excellent, biography by Lynde Phelps Wheeler corrects the general notion that he was an unappreciated scientist, born out of his time. He lived by choice a quiet contemplative life and he received, before the end of his life, as much recognition as a man of his type would desire. His published papers had the profound attention and respect of the other great savants of his generation. These included Maxwell, Boltzman, Ostwald, Lord Kelvin, J. J. Thompson, Nernst, and others. Michaelson looked to him as the man who would be most likely to explain his famous experiment with Morley, i.e., to discover relativity a quarter of century before Einstein did.

Gibbs' intensive fame is secure and growing. No books on thermodynamics, statistical mechanics, physical chemistry, or theoretical electrochemistry are written without reference to his fundamental work. However, few Americans even know the name of our greatest scientist. At very long last, Gibbs was elected to New York University's Hall of Fame. There is a pedestal ready to receive a bronze bust, but so far it is empty. In spite of appeals, funds have been slow in coming in to pay the sculptor. A contribution to The Electrochemical Society Gibbs Fund will help rectify this matter and will do a bit toward giving an extra dimension to the fame of the man of whom the members of The Electrochemical Society should be especially proud, both as Americans and as practitioners of a science to which Gibbs contributed important fundamental principles.

—D. A. MacInnes

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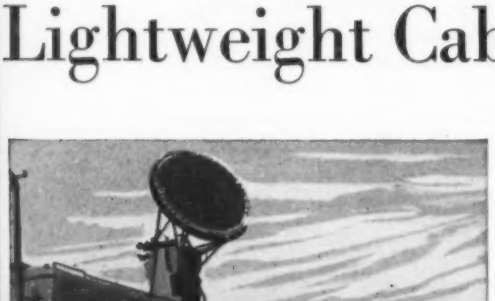

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Hans Thurnauer

Presidential Candidate

Hans Thurnauer, Head of the Inorganic Section of the Central Research Laboratory, Minnesota Mining and Manfacturing Company, St. Paul, Minn., has been a member of The Electrochemical Society since 1935. Born in 1908 in Nuremberg, Germany, he received his engineering degree in chemistry from The Charlottenburg Institute of Technology, Germany, in 1930, and received his M.Sc. degree in ceramic engineering, in this country, from the University of Illinois in 1931.

After returning to Europe, he worked as ceramic research engineer in German and British plants until he made his permanent residence in the United States in 1935. From 1935 until early this year he was connected with the American Lava Corporation, Chattanooga, Tenn., manufacturers of technical ceramics.

Mr. Thurnauer served as a member of the Technical Industrial Intelligence Committee, investigating ceramic plants in Germany after the war. He is the author of numerous articles on technical ceramics and holds various patents in this field. He has been active in furthering the interests of the Society in the field of technical ceramics both for dielectric and high temperature applications. He is a member of the Society's Finance Committee and Perkin Medal Committee.

William C. Gardiner

Vice-Presidential Candidate

William C. Gardiner was born in Exeter, Ontario, in 1904 and became a citizen of the United States in 1939. While he was an undergraduate at Queens University, Professor Dorrance persuaded him that power development on the St. Lawrence River would create a great demand for electrochemists. Accordingly he took a Master's degree working on an electroplating problem. He continued his electrochemical training at Princeton University under Professor G. A. Hulett. His thesis on the Weston Normal Cell was published in the TRANSACTIONS of The Electrochemical Society in 1929 and won for him the Society's first award of the Young Authors' Prize.

Dr. Gardiner spent three years as a Research Chemist for Comstock and Wescott, Inc., in Niagara Falls, working on chlorine metallurgy. Since 1932 he has worked on electrochemical research and development for Mathieson Alkali Works (now Olin Mathieson Chemical Corporation). His present position is Associate Director of Electrochemical Engineering in the Research and Development Division; his work has been with mercury type alkali-chlorine cells. He was active in the design, construction, and initial operation of plants using Mathieson cells at Arvida, Quebec, Saltville, Va., and McIntosh, Ala. He was captain of the U. S. chlorine industry team which toured German chlorine plants after World War II and brought back working drawings and detailed operating instructions of the best practice there. He also worked on the development of a cell to produce magnesium and chlorine from hydrated magnesium chloride feed. These cells were installed at the Mathieson Magnesium Plant in Lake Charles, La., where he was Superintendent of the Electrolytic Department. He holds patents on brine treatment, mercury cells, and magnesium cells and has published papers of interest to the electrolytic chlorine industry. He acts as consultant on electrochemical problems for several U. S. government projects.

Dr. Gardiner joined The Electrochemical Society in 1927 and has been active in the Niagara Falls Section, which he has served as Secretary-Treasurer and Chairman. He also served on convention committees when the Society met in the Buffalo-Niagara Falls area. He has been Chairman of the Industrial Electrolytic Division, and Divisional Editor of the JOURNAL since 1950. He has also been a member of the Alkali-Chlorine Committee.

John R. Musgrave

Vice-Presidential Candidate

John R. Musgrave, Chief Physicist in the Eagle-Picher Research Laboratories at Joplin, Missouri, was born at Reading, Pennsylvania, in 1906. He received his degree in chemical engineering at Lafayette College in 1927. Following a period of industrial research, he entered the graduate school of the University of Toronto. There he re-

JOHN R. MUSGRAVE

EUGENE WILLIHNGANZ

ceived the Ph.D. degree, majoring in physical chemistry, in 1933. Shortly after the completion of his graduate work, he became affiliated with the Eagle-Picher Research Laboratories, where he is, at present, in charge of the Physical-Chemical Section of the Laboratories.

Dr. Musgrave's research activities cover work on thermal insulation, storage batteries, paint, corrosion, instrumentation, diatomaceous earth, and rare metals. He has been active in the development of high-purity germanium for semiconductor work, as well as gallium. He holds several patents and is the author or coauthor of technical papers on storage battery technology, particle-size determination (in the subsieve range), germanium, and gallium.

Dr. Musgrave joined The Electrochemical Society in 1941 and has been particularly active in the Battery and Electronics Divisions. He has been Secretary-Treasurer and Chairman of the Electronics Division and has participated in the development of the rare metals and semiconductor symposia. He is at present a member of the Acheson Award Committee and the Chairman of the Membership Committee. He is also a member of a number of other scientific organizations.

Eugene Willihnganz

Vice-Presidential Candidate

Eugene Willihnganz was born in Beaver Dam, Wis., in 1903. He attended the University of Notre Dame where he studied organic chemistry under J. A. Nieuwland and did some of the early work on synthetic rubber derived from acetylene. He also completed the course in chemical engineering and graduated with an M.S. in 1925. After several years of industrial research dealing with dyestuffs and their intermediates for the Calco and Klipstein divisions of the American Cyanamid Company, he returned to school to study physical chemistry. He attended the Pennsylvania State College (now Pennsylvania State University) where, under the direction of J. G. Aston, he helped set up the low temperature laboratory and establish the University temperature scale in terms of a helium gas thermometer down to the triple point temperature of hydrogen. He received the Ph.D degree in 1934.

For the past 20 years he has been connected with the battery industry, first in charge of battery research for the National Lead Company and later as Director of Research for Gould-National Batteries, Inc., where at present he is Staff Consultant.

Dr. Willihnganz has been active in the Battery Division of the Society since the Division was organized more than ten years ago, and has watched it grow into an important part of the Society. He has organized several highly successful symposia on battery problems, and was Division Chairman from 1952 to 1954. As a member of the Board of Directors he has taken an active part in managing the affairs of the Society.

He has published a number of papers discussing storage battery reactions and has also supervised work on battery problems for the armed services. He is now trying to relate battery operating characteristics to the mechanism of electrode reactions, and admits that there are still many unsolved problems facing electrochemists.

DIVISION NEWS

Electronics Division

Semiconductor Symposium, May 1956

The fourth annual Semiconductor Symposium of The Electrochemical Society will be held on April 29, 30, and May 1, 2, and 3, 1956 at the Mark Hopkins Hotel in San Francisco, Calif. This notice is an invitation to submit papers for presentation. Early plans are to divide the sessions as follows:

(*A*) Two half-day sessions on semiconducting materials—elemental, alloys, and compounds.

(*B*) A half-day session on surface controlled phenomena.

(*C*) A half-day session on chemical process technology.

In each of the areas of interest we would like to present a balanced agenda including one review paper of the state of each field, 30-minute presentations (including discussion time) of new information which can be scheduled by midwinter 1955, and a number of shorter presentations of about 10 minutes' duration of the "late news" type.

If you wish to present papers, will you please notify the undersigned as follows:

(*A*) Signify interest in participating and title of proposed paper as early as possible, no later than November 15, 1955. Such information is needed for agenda planning purposes.

(*B*) Submit an abstract of approximately 75 words no later than January 2, 1956. This abstract will be printed in the general program for the meeting.

(*C*) Submit a second "extended abstract" of about 1000 words along with brief pertinent data, illustrations, curves, etc., not later than February 1, 1956. This extended abstract is "printed, but not published" in a booklet "Enlarged Abstracts of Papers Presented by the Electronics Division" and is available at the meeting at cost.

Plans for the ten-minute "late news" type of papers are as follows:

(*A*) Notify the General Chairman (writer of this notice) as soon as it appears likely that you will be able to present a "late news" paper, giving title or general area of interest.

(*B*) Submit 75-word abstracts no

later than April 8, 1956. These titles and abstracts will not be in the Meeting Program or the Enlarged Abstracts, but arrangements will be made to have mimeographed copies available prior to the meeting.

J. W. FAUST, JR.
(*1956 Chairman Semiconductor Symposium*)

Mailing Address:
Westinghouse Research Laboratorise
Beulah Road, Churchill Borough
Pittsburgh 35, Pa.

E & M Rare Earth Symposium, May 1956

The Electrothermics and Metallurgy Division is soliciting papers for the April 29–May 3, 1956 Society Meeting in San Francisco. The subject of one symposium will be "Rare Earths." Original papers are requested rather than reviews of previously reported studies. Also, a number of papers in the general field of chemical metallurgy are desired.

Authors who wish to present papers should submit a *75-word abstract* to W. H. Smith, General Electric Research Laboratory, P. O. Box 1088, Schenectady, N. Y., *not later than January 2, 1956.*

SECTION NEWS

Ontario-Quebec Section

At a technical meeting of the Ontario-Quebec Section held at McGill University on May 13, 1955, a total of 75 members and friends of the Society attended a symposium on "Titanium." Visitors were present from U. S. points as well as from Ontario and Quebec.

The Chairman, Dr. John Convey, explained that no formal papers were to be presented, but that each main speaker would outline developments in his particular field in as short a time as possible in order that the audience could participate in a general discussion. Dr. Convey, in introducing the subject of "Titanium," emphasized that the Canadian Government is interested in fostering the growth of a completely integrated titanium industry in Canada and has been assisting research in all phases.

The first speaker, Dr. G. G. Hatch, covered the preparation and smelting of raw materials at Sorel, P. Q. He described the Q. I. T. process for smelting ilmenite to produce a 72–74% TiO_2 slag and low carbon iron. The regular slag is used mainly for the production of paint pigments but an 80% TiO_2 slag is made as a raw material for titanium metal producers. In view of the cost differential between Sorel slag and rutile as a raw material it is felt that the TiO_2 slag has great promise for this use, though some development work will be necessary to fully evaluate its economies.

Dr. K. W. Downes described the work being done at the Mines Branch in Ottawa, particularly in regard to developing a commercial process to produce titanium metal by means of the reversible reaction $2TiCl_2$ Ti + $TiCl_4$. $TiCl_2$ is passed over titanium bearing sinter or aggregate at elevated temperatures and the $TiCl_4$ is removed as a volatile liquid or vapor, leaving metallic titanium in the form of a fine pyromorphic powder. As the reaction is reversible, special equipment and techniques are needed for recovery of the products. Dr. Downes suggested that, in view of the success that has been achieved with the similar aluminum reaction (Gross process), this method of producing titanium metal should hold promise. Dr. Downes noted that metal can be produced by dissolving $TiCl_2$ in fused sodium chloride and the metal plated out on nickel-plated iron cathodes, releasing $TiCl_4$, which is recycled.

Mr. H. A. Timm of the Dominion Magnesium Company discussed briefly the general advantages of the oxide or direct reduction process. Starting with a pure oxide the metallic titanium may be alloyed with various metals and high titanium master batch alloys produced for addition to other metals. Mr. Timm claimed that alloys produced in this way could be produced as cheaply or cheaper than by starting with titanium produced by the Kroll process. Mr. Timm discussed the properties required in titanium alloys. He pointed out that in powder metallurgy applications the Domag powder could be prepared for use by crushing, whereas the malleable titanium produced by other methods could not.

Mr. M. R. Fasken of the Shawinigan Water & Power Company described briefly Shawinigan's method of producing metal electrolytically by the electrolysis of $TiCl_4$ in a bath of fused chlorides. Shawinigan prepares $TiCl_4$ from Q. I. T. TiO_2 slag by conventional methods. Water white $TiCl_4$ is dissolved in a fused salt bath. Unfortunately, Mr. Fasken was not at liberty to do more than say that electrolysis was carried out in a fused salt bath. He commented on the constantly changing Brinnell requirements for metal and stated that Shawinigan could produce metal of 110 Brinnell.

Dr. H. V. Kinsey of the Mines Branch, Ottawa, dealt with the effects of impurities in titanium metal. He gave permissible limits and pointed out that oxygen could only be lowered by dilution, whereas hydrogen can be removed by vacuum treatment. Oxygen and carbon are the most serious contaminants. Dr. Kinsey gave the following limits for contaminants: O_2, 0.1% max.; N, 0.04% max.; H_2, 0.01% max.; C, 0.06% max.; Fe, 0.05% max.

Dr. Convey commented that Canadian universities were engaged in titanium research and mentioned particularly that Laval University is doing work on TiO_2 in fused electrolytes, the University of Toronto on oxidation rates, and the University of British Columbia on titanium base alloys.

Dr. Wurm of Laval University gave a short outline of the work on fused electrolytes. When lithium and calcium are added as chlorides, these metals are deposited before titanium.

Following the above presentations, members of the audience participated in a lively discussion and question period.

Prior to the technical meeting, the annual meeting of the Section was held at which the following officers were elected for the 1955–1956 season:

Honorary Chairman—A. F. G. Cadenhead
Chairman—P. J. Ensio
Vice-Chairman (Program)—A. C. Holm
Vice-Chairman (Membership)—John Sumner
Secretary-Treasurer—R. R. Rogers, 568 Booth St., Ottawa, Ont., Canada
Representatives on Council of Local Sections—P. J. Ensio and R. R. Rogers

R. R. ROGERS, *Secretary-Treasurer*

PERSONALS

DANIEL D. ZIELIK is no longer with the Machlett Laboratories, Inc., Springdale, Conn., where he was a metallurgical chemist in the x-ray and special electronic tube field. He recently established his own organization, known as The Precious Metals Platers, in Fairfield, Conn. The organization will offer

electroplating services to the instrumentation and electronics fields, as specialists in the heavy precision electrodeposits of the precious and platinum group metals, silver, gold, palladium, and rhodium.

PAUL RUETSCHI

PAUL RUETSCHI, formerly of Schafisheim, Aargau, Switzerland, has joined the Research Dept. of the Electric Storage Battery Co. in Philadelphia, Pa., as a research physical chemist.

TIMO HEILALA recently was advanced to production manager in charge of all processes at the Calvert City, Ky., works of the Pennsylvania Salt Manufacturing Co. He had been area supervisor of the chlor-caustic and anhydrous hydrochloric acid plants.

CLAIRE H. FELLOWS, Detroit Edison Co., Detroit, has been elected President of the American Society for Testing Materials for a one-year term, and F. L. LAQUE, The International Nickel Co., Inc., New York, has been elected Director of the ASTM for a three-year term.

M. S. THACKER recently assumed charge of his new office with the Government of India as Director, Council of Scientific and Industrial Research, Delhi. He was previously Director of the Indian Institute of Science in Bangalore.

BERNARD A. GRUBER, formerly associated with the Ethyl Corp. in Baton Rouge, La., is now with the Research and Engineering Div. of the Monsanto Chemical Co. in Dayton, Ohio.

HANS THURNAUER, previously vice-president and director of research at the American Lava Corp., Chattanooga, Tenn., has joined the Minnesota Mining and Manufacturing Co., St. Paul, Minn., as Head of the Inorganic Section of the Central Research Laboratory.

WAYNE O. GRAFF

Wayne O. Graff, Plant Manager at the General Electric Company's Chemical Products Works in Cleveland, Ohio, died on Thursday, July 7, at the age of 37 years.

With 14 brothers and sisters, Wayne Graff grew up in New Philadelphia, Ohio. After receiving his degree in chemical engineering at the Carnegie Institute of Technology, he joined the Lamp Division of the General Electric Company at Nela Park, Cleveland, in 1940. Following several engineering assignments at the Cuyahoga Lamp Works and at the Lamp Development Laboratory, he became Chief Quality Engineer in 1948 and later Plant Superintendent at the Chemical Products Plant. In 1953 Mr. Graff was appointed Supervisor of Production and Personnel for the Parts Manufacturing Department of the Lamp Division. In January 1955 he returned to Chemical Products as Plant Manager.

Mr. Graff was a member of The Electrochemical Society since 1941 and a former Chairman of the Cleveland Section.

Surviving him are his wife, Lillian, and two young sons.

His untimely passing brought to a close an all-too-brief, but promising, career.

GAR A. ROUSH

Gar A. Roush, Emeritus Member of the Society, died at his home in Arlington, Va., on August 16, 1955. He was 72 years old.

He was born in Gas City, Ind., in 1883, and was graduated from Indiana University, later receiving the master's degree from the University of Wisconsin. He joined the staff of Lehigh University as Assistant Professor of Metallurgy in 1912 and was Associate Professor from 1920 to 1926. He was editor of *The Mineral Industry*, an annual published by McGraw-Hill Book Company, New York, from 1913 to 1943. During World War I he served as captain in the Ordnance Department, U. S. Army, and later became major in the Staff Specialist Reserve. He was awarded the Toulmin medal of the Society of American Military Engineers in 1939. In 1943 he moved to Washington, D. C., to become mineral technologist in the U. S. Bureau of Mines, and at the time of his death was connected with the U. S. Treasury Department in the Bureau of Federal Supply, Strategic and Critical Materials Division.

Mr. Roush joined The Electrochemical Society in 1904 and was Assistant Secretary under Joseph W. Richards from 1912 to 1918. He was also a member of the American Institute of Mining and Metallurgical Engineers and the Society of American Military Engineers. He was the author of numerous scientific articles.

He is survived by his wife, the former Lillian Coleman, and a sister, Stella, of Jonesboro, Ind.

WENDELL MITCHELL LATIMER

Wendell Mitchell Latimer, professor of chemistry at the University of California and chemical division director of the Atomic Energy Commission's Livermore Laboratory, died on July 6, 1955 at the age of 62.

He was born in Garnett, Kan., and was graduated from the University of Kansas in 1915. He received his Ph.D. degree in chemistry at California in 1919, at which time he joined the staff of the University of California in Berkeley.

His early work with liquefied hydrogen in low temperature thermodynamics was credited with inspiring the work which won a Nobel Prize for William Giauque. He was also credited with doing much to inspire Glenn Seaborg and Willard Libby in their discovery of methods for separating plutonium from uranium. He did much of the primary chemical research which produced the targets and bullets for Ernest O. Lawrence's various atom smashing machines.

Dr. Latimer had been a member of The Electrochemical Society since 1939.

LETTER TO THE EDITOR

Dear Sir:

The theory of corrosion inhibition by strictly cathodic inhibitors described in my paper, "A Theoretical Basis for a New Method of Investigating Corrosion Inhibition," in the April 1955 JOURNAL can be extended to encompass inhibition by strictly anodic agents as well. This fact increases the usefulness of the theory, but at the same time disproves a conjecture made in the paper regarding composite anodic-cathodic agents. In the development that follows, equations and inequalities

bearing numbers less than 47 are identical to the correspondingly numbered relationships in the above-cited paper. Those bearing higher numbers are new.

It is easy to verify that in the j^{th} local cell,

$$-E_{1j} + I_{1j}R_{1j} = -I_{2j}R_{2j} - E_{2j} \quad [47]$$

Combining equations (5) and (47) and differentiating,

$$d\Gamma = -dE_{2j} - I_{2j}\,dR_{2j} - R_{2j}\,dI_{2j} - W\,dI_3 \quad [48]$$

Define:

$$\tau_j = \frac{\partial E_{2j}}{\partial x} + I_{2j}\frac{\partial R_{2j}}{\partial x} \quad [49]$$

Note that when the inhibitor under consideration is strictly anodic τ_j is zero. Upon substitution of the value of dI_{2j} given by the equation following (11) and the values of dE_{2j} and dR_{2j} given by (9) in equation (48); and then using the definitions of τ_j and μ_j given by (49) and (13), there results

$$d\Gamma = -\tau_j\,dx - \mu_j(dI_{1j} + dI_{3j}) - W\,dI_3 \quad [50]$$

By substituting first the value of dI_{1j} given by equation (17) and then the value of dI_{3j} given by equation (23), in equation (50) one can deduce the relationship:

$$d\Gamma = -\left(\tau_j + \mu_j\frac{\partial I_{1j}}{\partial x}\right)dx + \mu_j I_3(\Delta_j - 1)\,dH_j + [\mu_j H_j(\Delta_j - 1) - W]\,dI_3 \quad [51]$$

This equation is completely equivalent to equation (24), but is expressed in a form more convenient for the present purpose. From equation (51) can be deduced immediately expressions for $\partial\Gamma/\partial x$ and $\partial L/\partial I_3$ equivalent to equations (25) and (26). When μ_j is eliminated between these two expressions and the resulting relationship solved for $\partial I_{1j}/\partial x$ the result is an equation identical to (27) except that $(\Delta_j - 1)$ replaces Δ_j and τ_j replaces ψ_j. From this an equation analogous to (39) can be derived; then essentially the same statistical argument that was used in the derivation of equation (40) yields the result:

$$\frac{\partial I_1}{\partial x} = \frac{-\frac{\partial\Gamma}{\partial x}\sum_{j=1}^{N}(\Delta_j - 1)H_j - \sum_{j=1}^{N}(\Delta_j - 1)H_j\tau_j}{\frac{\partial\Gamma}{\partial I_3} + W} \quad [52]$$

Equations (40) and (52) are completely equivalent.

In the case of a strictly anodic inhibitor, $\tau_j = 0$ for every value of j as was mentioned earlier. Therefore, for that type of agent, the second sum in the numerator of the right-hand member of equation (52) is zero. Also $0 \leq \Delta_j \leq 1$ implies $-1 \leq (\Delta_j - 1) \leq 0$; therefore $|(\Delta_j - 1)| \leq 1$. These two facts together with equation (20) make possible the deduction of the inequality (43) from equation (52). Hence, that inequality, derived previously for strictly cathodic inhibitors, is also valid for strictly anodic inhibitors. This means that in cases in which $\left|\frac{\partial\Gamma}{\partial x}\right| \div \left|\frac{\partial\Gamma}{\partial I_3} + W\right|$ is small the agent under test is neither a good strictly cathodic nor a good strictly anodic inhibitor. Therefore, if it is an inhibitor at all it must function both at the local anodes and local cathodes. It can also be shown by simple example that this result implies that the writer's surmise that inequality (43) can be used to estimate the effectiveness of the "cathode component" of a composite anodic-cathodic inhibitor is incorrect. The method is applicable only to strictly cathodic and strictly anodic agents.

James G. Jewell
Gulf Research & Development Co.
Pittsburgh, Pa.

BOOK REVIEWS

The Elements of Chromatography by T. I. Williams. Published by the Philosophical Library, Inc., New York, 1954. vii + 90 pages, $3.75.

This slim volume presents a brief introduction to and survey of the current state of development of the chromatographic technique. The work is intended to "prove useful both to students in the universities, where chromatography is now finding a long overdue place in the syllabus, and to the postgraduate research worker who requires a general survey of the method as practiced today." For such as these, this volume is heartily recommended. The author writes with an admirable clarity of style and felicity of expression, and the choice of figures and illustrations (seven in full color) is truly excellent. The printing is good, the paper is high quality, and there are very few typographical errors.

Apart from a fine historical survey in which the author provides a more realistic assessment of the relative importance of the contributions made to this field by the several early workers than will be found in most other volumes on this subject, there is little in this book that will not be already familiar to the average research worker who has, over the past ten years, read several review articles or listened to occasional lectures dealing with chromatography. Adsorption, partition, and ion exchange chromatography are briefly described, and the general behavior of adsorbents and solvents is summarized. The apparatus and laboratory techniques in common use for colored and for colorless substances are presented, and the procedures available for development of the chromatogram are described and illustrated. The final chapter discusses the possibilities inherent in the adaptation of the chromatographic technique on an industrial scale.

Because of its brevity, this work is recommended only to those who know very little about chromatographic techniques, but for this group it should serve as an excellent introduction to the subject. It is regrettable that the inclusion of the aesthetically very pleasing chromatograms in color has caused the purchase price of so small a book to be so high.

S. Z. Lewin

Manganese, Metallurgy of the Rarer Metals, Number 3, by A. H. Sully. Published by Academic Press Inc., New York, 1955. 305 pages, $6.50.

It is surprising to find that a series on the metallurgy of the rarer metals includes a book on manganese. If we take price as a measure of rarity, then the approximately 30 cents per pound for manganese places it between magnesium and copper, neither of which is considered as particularly rare. Further-

1956 BOUND VOLUMES

Members and subscribers who wish to receive bound copies of Vol. 103 (for 1956) can receive the volume for the low, prepublication price of $6.00 if their orders are received at Society Headquarters, 216 West 102nd St., New York 25, N. Y., by *December 1*. After that date members will be charged $12.00 and nonmembers, including subscribers, $18.00.

more, it has been suggested that price reductions which would result from increased production would make manganese one of the least costly nonferrous metals. The only justification for including manganese with the rare metals is that until about 15 years ago high-purity manganese metal was indeed very rare. With the commercial exploitation of the electrolytic process developed at the U. S. Bureau of Mines, this last element of rarity has been eliminated.

It is, in fact, the present availability of manganese that makes this book welcome at this time; since, by focussing attention on the metal and disseminating the most recent information on its properties, new uses for it may be developed. Apart from its inclusion in a series on rare metals, the book itself is a valuable contribution to metallurgical literature. It is well written, succinct, and, for a comparatively small volume, contains a very thorough survey of its field. Where details have been omitted or cursorily treated, references are usually supplied in the adequate bibliography which concludes each chapter. Very few errors were noted by the reviewer, though one is rather serious. On page 67, in a discussion of the difficulties in the electrowinning process for manganese, a misleading reason is given for the use of diaphragms in the electrolytic cells. It is stated that "It is necessary to use a diaphragm cell for the (electro) deposition since manganese cannot be leached from its ores by alkaline solutions and cannot be plated from acid solutions." The preparation of suitable leaching and plating solutions may be readily accomplished by proper *p*H adjustments at the correct stages of the process without the use of diaphragms. Actually, diaphragms are used in the cell to prevent the anode sludge from being incorporated in the cathodes, and to minimize oxidation of the catholyte.

Sully emphasizes that although manganese ores are abundant they are usually present in the wrong places with respect to their most important use, the manufacture of steel. In fact, the only important steel-making country which is independent of imported manganese is the U.S.S.R. The subject of this chapter is therefore of great political as well as technical interest. After observing that about 70% of the manganese consumed by the steel industry is wasted, excellent summaries of a number of processes for the recovery of manganese from slags are given. Also included are descriptions of processes for recovery of manganese from low grade ores.

The two chapters on the physical properties of manganese and the constitution and properties of manganese alloys constitute over one-half the book and are exhaustive and critical compilations of available data. The complex crystal structures of the allotropic forms of manganese are particularly well treated.

In the chapter on alloys, phase diagrams are reproduced and discussed, and considerable crystallographic data are given for 45 binary alloys and 22 ternary alloys of manganese. The reviewer felt that, had space permitted, fuller treatment of the physical and mechanical properties of the alloys would have been desirable.

In the last chapter of the book there are brief discussions of the workability of manganese, electroplating of manganese, vapor phase "manganization," and oxidation of manganese at high temperatures. Since only ten pages are devoted to this final chapter its greatest value will probably be as a bibliographic source for these miscellaneous subjects.

In general, this book contains much material not elsewhere available, except from the original literature in several languages, and will, in the reviewer's opinion, prove to be a valuable reference work on the metallurgy of manganese.

S. Senderoff

Storage Batteries, Fourth Edition, by George Wood Vinal. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York, 1955. 446 pages, $10.00.

This new edition of the well-known treatise on secondary batteries is unchanged in scope. It approaches the subject of secondary batteries in the general fashion of the third edition, encompassing the chemical and physical principles of battery operation, engineering applications, materials of manufacture, and manufacturing processes, without becoming highly technical. The most pronounced changes are the inclusion of a new short section on the silver-oxide secondary cell, the promotion of battery additives to a chapter section, and the discussion of the new selenium and magnesium-copper sulfide rectifiers.

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In the 15 years since the previous edition was published the battery industry has seen many new developments, the impetus for these being given largely by military necessity. The dollar value of batteries manufactured has more than trebled since the 1925–1937 period. The nickel-cadmium battery is being produced in this country, and the silver oxide cell is now used as a secondary cell. These and many other changes of a less major nature are considered. New research work has been recognized and is well referenced. Many new illustrations are included and the photographic reproductions are better.

Some portions of the third edition have been omitted, but most of the material has been carried over, largely intact. Certain redundancies were eliminated. One misprint was noted. On page 34, in the discussion of the basic sulfates, the book states that the tetrabasic sulfate occurs at high temperatures. While this is not untrue, it was meant to say that the dibasic sulfate occurs at high temperatures.

To the man working in the research fields concerned, the treatment of the section on discharge mechanisms, grid corrosion and growth in the lead-acid cell, and measurement of battery resistance leaves something to be desired. That is to say, these areas are still either highly conjectural or open to interpretation. Adequate treatment of these topics is, however, outside the scope of the book, because highly technical discussion would be required.

The book remains perhaps the best general treatise in the secondary battery field. A newcomer to battery work could not do better than read and study this book for rapid orientation. It also serves as a very handy reference book for properties of battery materials and battery discharge characteristics.

JOHN J. LANDER

NEWS ITEMS

Sustaining Member

The Carborundum Company, Niagara Falls, N. Y., has been reinstated as a Sustaining Member of the Society as of August 30.

New Solvay Plant

Solvay Process Division, Allied Chemical & Dye Corporation, has announced that it will shortly begin construction of a mercury cell chlorine-caustic soda plant on property recently purchased near Brunswick, Ga. The 700 acre site is situated on the Turtle River, north of Brunswick. The new Solvay plant is expected to be in production by December 1956.

Initially the plant will provide employment for about 125 people and will have the capacity to produce 100 tons of chlorine and 125 tons of caustic soda per day. At full operation, annual sales value of products to be manufactured in the new plant would be in excess of $4,000,000. Electric power required for operations will be purchased from the Georgia Power Company.

National Research Corp. Titanium Plant

National Research Corporation has received a contract for $1,183,495 from the General Services Administration to finance construction and operation of a demonstration pilot plant for production of titanium metal by a new non-Kroll process developed by the company. The plant, which is being designed for 1000 lb of metal per day, will be housed in a building being erected near the site of the company's Equipment Division in Newton, Mass. The process, which has been in operation on a small pilot plant scale in Cambridge for two years under a joint program with Monsanto Chemical Company, produces metal of high purity in crystalline form.

Mr. James L. Vaughan, director of Process Engineering at National, will be responsible for general supervision of the program. Dr. Wayne H. Keller, director of the Chemistry Department at National, will be in charge of plant operation.

Perkin-Elmer Forms New Subsidiary

The establishment of Nuclear Magnetics Corporation as a new subsidiary of The Perkin-Elmer Corporation has been announced.

The newly formed corporation will maintain executive offices and research and development facilities in Boston. Manufacturing operations will be transferred to the parent corporation's plant in Norwalk, Conn.

The Nuclear Magnetics Corporation will market a complete line of nuclear magnetic resonance equipment. It has purchased the complete rights to the NUMAR line from Laboratory of Electronics, Inc., Boston, designers and manufacturers of electronic equipment.

ASTM Committee on Electronics Materials

A new committee on electronics materials was authorized by the Directors of the American Society for Testing Materials in May to cover the field of materials for electron tubes and semiconductor devices.

The new committee, designated F-1 on Materials for Electron Tubes and Semiconductor Devices, will be concerned with materials for electron tubes such as grid wires, cathodes, mica

Physical Chemists, Electrochemists, or Chemical Engineers

Physical Chemists, Electrochemists, or Chemical Engineers with training in physical chemistry wanted for research and development. Work will involve laboratory studies of the fundamentals of corrosion chemistry, and analysis of practical corrosion problems that arise in all phases of the petroleum industry. Interest both in fundamentals and in engineering applications necessary. Corrosion experience and knowledge of statistics helpful but not required.

Address: **GULF RESEARCH & DEVELOPMENT COMPANY**
P. O. Drawer 2038
Pittsburgh 30, Pennsylvania

stampings, glass-to-metal seals and luminescent materials used in cathode ray tubes and in fluorescent lighting. In view of its concern with many different materials, the new committee will be working closely with several other technical committees of the Society.

The new committee was created from a nucleus consisting of Subcommittee VIII on Metallic Materials for Radio Tubes and Incandescent Lamps of Committee B-4 on Metals for Electrical Heating, Electrical Resistance, and Electronic Applications, which had for some time carried out considerable research and developed a number of standards on materials for electron tubes. It was obvious that with the expanding use of these materials a new committee with a scope covering electronic materials was desirable. Committee B-4 on Metallic Materials for Electrical Heating, Electrical Resistance, and Electrical Contacts will continue with a reduced scope.

The officers of Committee F-1 are: S. A. Standing, Chairman, Raytheon Manufacturing Co., Quincy, Mass.; F. J. Biondi, Vice-Chairman, Bell Telephone Labs., Murray Hill, N. J.; and S. Umbreit, Secretary, RCA Victor Div., Radio Corp. of America, Harrison, N. J. The new committee held its first official meeting on June 27 and 28 on the occasion of the Society's 58th Annual Meeting at Atlantic City, N. J. Mr. Standing and Mr. Umbreit were Chairman and Secretary, respectively, of Committee B-4.

Silicon Power Rectifier

Bell Telephone Laboratories recently announced the development of a silicon power rectifier capable of operating at currents 5000 times greater than conventional rectifiers of the same size. Two of these units, each the size of a pea when mounted on a cooling fin, can act as a full wave-rectifier providing more than 20 amperes of direct current at 100 volts, an output of 2000 watts, with only 20 watts lost as heat. The active portion of each unit is a silicon wafer one-tenth of an inch square and 5 mils thick.

"Atoms-for-Peace" Parley

U. S. and foreign engineers, scientists, and industrial representatives from 24 business and technical societies, 16 universities, 13 government bureaus and AEC contractors, and 34 major U. S. industrial corporations will present nearly 300 papers in 50 sessions in one week covering practically every phase of peacetime uses of atomic energy and its by-products at the Nuclear Engineering and Science Congress in Cleveland, December 12 through 16.

Coordinating the arrangements for the Congress is the Engineers Joint Council under the leadership of Thorndike Saville, Dean of the College of Engineering, New York University, and President of EJC.

Volumes Wanted

Will anyone who has a copy he no longer needs of Vol. 86 (1944) and 92 (1947) of the TRANSACTIONS please contact Toshio Keta, 4307 Sheridan St., University Park, Hyattsville, Md.

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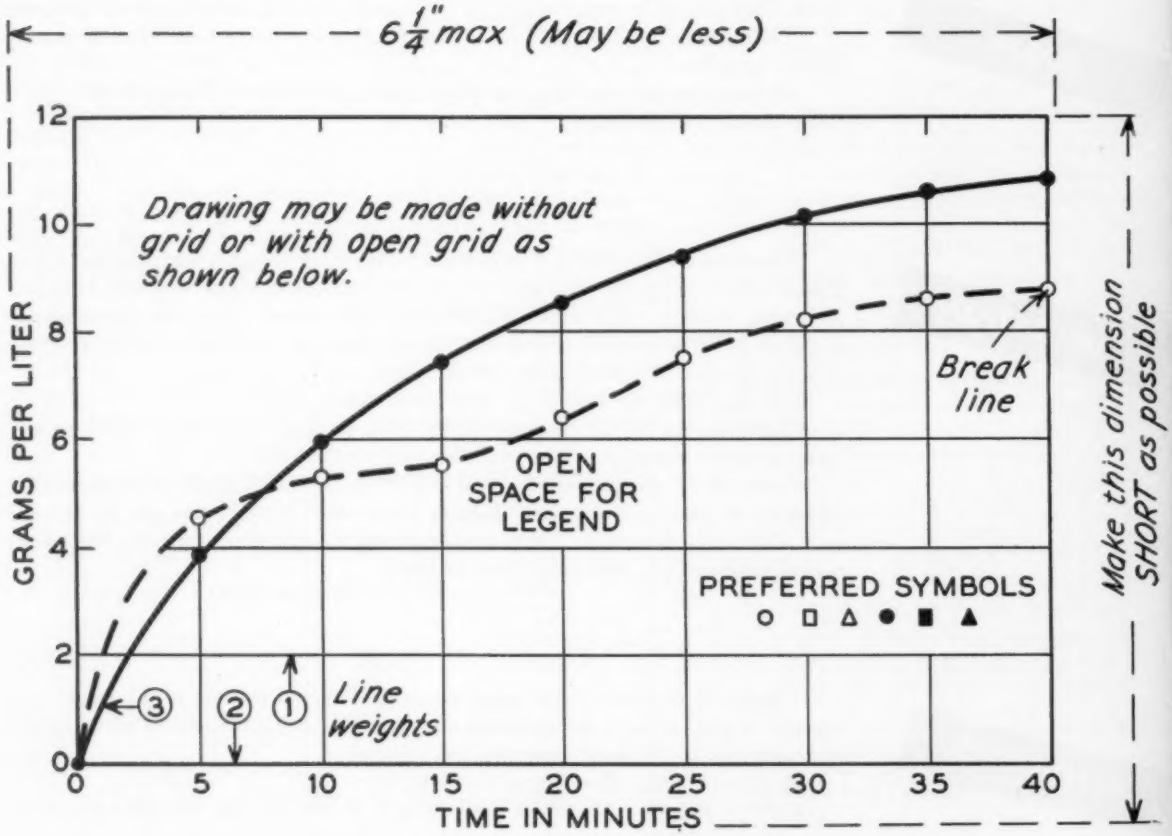

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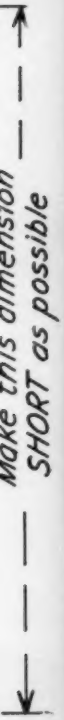

Formation of Manganese(II) Ion in the Discharge of the Manganese Dioxide Electrode[1]

A. M. Chreitzberg, Jr., D. R. Allenson, and W. C. Vosburgh

Duke University, Durham, North Carolina

ABSTRACT

In the discharge of electrodeposited manganese dioxide electrodes in ammonium chloride electrolyte at *p*H 7, very little manganese(II) ion enters the solution during the first third of the discharge, but it appears at an increasing rate thereafter. The effects of current density, *p*H, ammonium chloride concentration, and interruption of the discharge were studied. A mechanism is suggested involving the assumptions that the electrode reaction takes place on the exterior surface of the manganese dioxide and that the primary product is a lower oxide, which reacts with the electrolyte to give the manganese(II) ion formed. Additional evidence is presented for the first assumption.

Introduction

It was shown (1, 2) that manganese(II) ion is a product of the discharge of the manganese dioxide electrode. With a large volume of electrolyte and low *p*H (less than 4) it may be the only manganese-containing product (1). When electrodes made by electrodeposition of manganese dioxide on graphite are discharged at *p*H 7, the ion is produced in considerable quantity, but the main product is an oxide (2). When the discharge is continued to a cut-off value of zero against the saturated calomel electrode, the oxide has a composition of about $MnO_{1.6}$

Two different hypotheses may be made concerning the mechanism of manganese(II) ion formation: (*A*) the ion is the primary product of the electrode reaction, and it may take part in a secondary reaction with manganese dioxide, giving the oxyhydroxide, MnOOH (1); (*B*) a lower oxide is the primary product, and this reacts with the electrolyte, giving manganese(II) ion and a higher oxide in accordance with one of the following equations:

$$2MnOOH + 2H^+ \rightleftarrows Mn^{++} + MnO_2 + 2H_2O \quad (I)$$

$$Mn_3O_4 + 2H^+ \rightleftarrows Mn^{++} + 2MnOOH \quad (II)$$

Formation of manganese(II) ion was investigated further with results that are in better accord with the second hypothesis. Results can be correlated with the theory of the reaction mechanism previously proposed (3).

Experimental

Electrodes were prepared by electrodeposition of manganese dioxide on graphite rods of 0.48 cm diameter and 8 cm^2 surface area from an acid sulfate bath at 75°–90°C for 30 min with a current of 25 ma (3). This procedure gave a deposit with about 0.2 millimole of total manganese (2). The electrodes were washed thoroughly with water (2) and kept immersed in a solution of 2M ammonium chloride and 0.5M ammonia (*p*H = 8.8) for a week. They were then stored until used in the electrolyte to be used in the cells.

For discharge, an electrode was mounted in a central position in a glass vessel of 200-ml capacity with a cylindrical silver anode fitted around the inside wall. This had been coated with silver chloride in previous work. A Luggin capillary with its tip at a distance from the electrode approximately two to four times the tip diameter (4) allowed measurement against a saturated calomel reference electrode. Except as otherwise noted, the electrolyte was 190 ml of 2M ammonium chloride solution containing enough ammonia to give a *p*H of 7.3, about 0.01 mole/l.

For regulation of the temperature during discharge, the cells were placed in a test cabinet maintained at 25° ± 0.5°C. Purified nitrogen that had been washed with some of the electrolyte was passed through the cell electrolyte during discharge to provide an inert atmosphere and for stirring. Occasional checks of the *p*H showed that no appreciable changes occurred.

Electrodes were discharged by passage of an approximately constant current through the cells. Current was measured in terms of potential drop across a known resistance. Current and potential against the calomel electrode were measured and recorded continuously during a discharge by a L&N Speedomax, x_1, x_2 recording potentiometer.

Samples of the electrolyte of 10 ml each were

[1] Manuscript received October 18, 1954. This paper was prepared for delivery before the Boston Meeting, October 3 to 7, 1954.

taken at intervals during the discharge and replaced with equal volumes of fresh electrolyte to keep the total volume constant. Manganese was determined in each sample colorimetrically as permanganate after evaporation with sulfuric and nitric acids and oxidation with periodate. At the end of the discharge manganese was titrated potentiometrically in the entire electrolyte, after addition of pyrophosphate. The two methods agreed satisfactorily. In calculating the manganese(II) ion produced in the discharge, correction was made for the manganese content of the samples removed.

Some of the discharges were allowed to proceed continuously to the end, and some were interrupted at intervals. In the latter case, a sample was taken immediately after each interruption and another after the cell had stood on open circuit for 24 hr. The circuit was kept open for 24 hr after each interruption, then the discharge was continued. Some similar discharges, but without the manganese determinations, were made by Ferrell and Vosburgh (3) and the results are shown in their Fig. 6 and 7. The present data were quite similar.

Results and Discussion

The amounts of manganese(II) ion formed in several discharges are shown in Fig. 1. The manganese ion found in the electrolyte, in hundredths of millimoles, is plotted against the amount of discharge in milliampere-minutes. It can be seen that at *p*H 5 in the presence of zinc the formation of manganese(II) ion starts at the beginning of the discharge and continues at a slowly increasing rate throughout.

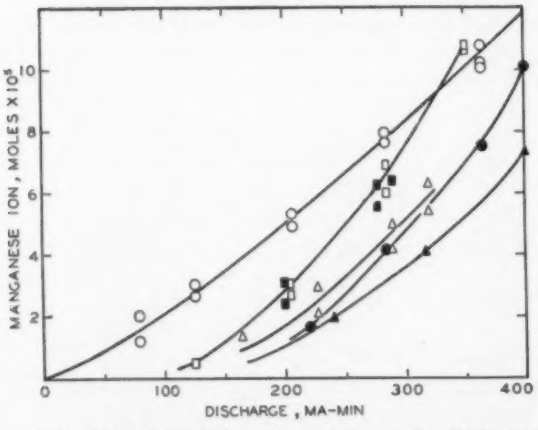

Fig. 1. Manganese(II) ion formed during the discharges of manganese dioxide electrodes. ○—Interrupted discharge with $ZnCl_2$ at *p*H 5, current density 0.1 ma/cm²; □ and ■—two similar interrupted discharges at *p*H 7.3 showing reproducibility, 0.1 ma/cm²; △—interrupted discharge at *p*H 7.3, 0.4 ma/cm²; ●—continuous discharge at *p*H 7.5, 0.025 ma/cm²; ▲—continuous discharge at *p*H 7.4, 0.05 ma/cm².

TABLE I. *Total manganese(II) ion produced in various discharges; pH 7*

Current	Capacity	Type of discharge	Manganese(II) ion	
			Observed	Calculated*
ma/cm²	*ma-min*		*mmoles*	*mmoles*
0.025	400	Continuous	0.100	0.125
0.05	400	Continuous	0.074	0.125
0.1	383	Continuous	0.055†	0.119
0.2	358	Continuous	0.039	0.112
0.4	346	Continuous	0.033	0.108
0.025	367	Interrupted	0.098	0.114
0.1	350	Interrupted	0.108	0.109
0.1	290	Interrupted	0.066	0.090
0.4	393	Interrupted	0.100	0.122
0.4	320	Interrupted	0.064	0.100

* Calculated from the capacity as if manganese(II) ion were the only product.

† Ammonium sulfate electrolyte.

At *p*H 7 without zinc, no measurable manganese(II) ion was found in the electrolyte until after 100 ma-min. Manganese(II) ion was formed at an increasing rate throughout the remainder of the discharge.

On the curves for interrupted discharges, two manganese ion values are usually given for each milliampere-minute value, with the curve passing between them. The lower of the two manganese ion values is the amount found immediately after breaking the circuit, and the higher is the amount found 24 hr later, the circuit having been open and the nitrogen atmosphere maintained during the 24 hr. In interrupted discharges the manganese ion concentration nearly always increased during the period of open circuit, and a decrease was never observed.

Data of Fig. 1 are typical. Several other discharges agreed with those shown, but were omitted from Fig. 1 to avoid confusion. Total amounts of manganese in solution at the ends of the discharges, current densities, and capacities for the discharges at *p*H 7 are given in Table I.

In the last four lines of the table the reproducibility appears poor, but the lower amounts of manganese were obtained from electrodes giving abnormally low electrical capacities. Up to the points at which these latter electrodes became discharged, they agreed fairly well in manganese in solution with their duplicates. This is shown for the 0.1 ma/cm² discharges in Fig. 1.

The last column of Table I shows how closely the amount of manganese(II) ion formed approaches the amount calculated as if this were the only product. In one of the interrupted discharges practically the theoretical amount was formed. In the other discharges 30–86% of the theoretical amount was formed. Some discharges at *p*H 5 which were cut off at 125 ma-min gave an average of 0.040 ± 0.002 m mole of manganese(II) ion with no regular variation

with current density (theoretical amount, 0.039 m moles).

Fig. 1 and Table I show that the more rapid continuous discharges gave less manganese in solution than the slower ones. Also, more manganese was formed in solution by the interrupted discharges than in all but the slowest continuous ones.

Absence of manganese(II) ion in the electrolyte in the first part of the discharge at *p*H 7 suggests that an oxide is the primary product of the discharge. The manganese(II) ion may be assumed to be formed by reaction of the oxide with the electrolyte when conditions are favorable.

Because of the importance of this conclusion an additional check in the early part of a discharge was made with more efficient stirring of the electrolyte. With stirring by a magnetic stirrer, no manganese(II) ion was detected after 20 ma-min of discharge, and a faint trace, about 2×10^{-6}M, was present after 40 ma-min.

Another check on the above theory is to inquire whether the lower manganese oxides, especially the oxyhydroxide and trimanganese tetroxide, do in fact react with an ammonium chloride solution of *p*H 7 or above. Samples of these two oxides prepared by precipitation (5) and having nearly the correct composition were available. These were washed repeatedly by stirring with water and decantation (as the analytical samples had been washed when the composition was determined) until excess manganese(II) salts were removed and a colorimetric test for manganese gave constant results with further washing. Then water in which the oxyhydroxide had been stirred for some time gave no trace of manganese in the test, while water stirred with trimanganese tetroxide for 2 hr gave a faint trace. On stirring with 1M ammonium sulfate (of *p*H 7.0) the oxyhydroxide gave a trace of manganese, about 7×10^{-6}M, and the trimanganese tetroxide gave 1.2×10^{-4}M after 2 hr stirring. The latter increased further with time. These experiments were carried out at about 30°C.

Reaction of trimanganese tetroxide with an ammonium sulfate solution seems to be slow. It may be assumed that the similar formation of manganese(II) ion from a reduced manganese dioxide surface is also slow. This suggests an explanation of some of the above observations. More manganese(II) ion is formed in a slow, continuous discharge than in a fast one because there is more time. The amount dissolved is not proportional to time because the closed-circuit electrode potential is higher in the slower discharges, corresponding to less reduction at the surface. More manganese(II) ion is dissolved in intermittent discharges than in continuous, because the dissolving process goes on during the period of interruption, or at least during the first part of the period. On prolonged standing on open circuit the process should be reversed; equilibrium conditions require that at *p*H 7 the manganese(II) ion return to the electrode.

$$MnO_2 + Mn^{++} + 2OH^- \rightarrow 2MnOOH \quad (III)$$

The theory of the discharge can now be made a little more detailed. In the early part of a discharge at *p*H 7, and in the absence of zinc ion, the primary reaction product is probably manganese(III) oxyhydroxide. It is probable that this is formed on the exterior surface of the manganese dioxide. Later in the discharge the oxyhydroxide is reduced further. Reduction of part of the manganese(III) ions at the surface to manganese(II) (with an accompanying decrease of oxide ion, or change to hydroxide) would give a surface resembling that of trimanganese tetroxide, subject to attack by the electrolyte.

When the circuit is broken in the latter part of the discharge, the electrode still has on its surface some manganese(II) ions which may disappear in two ways. (*A*) They may go into solution, accompanied by oxide or hydroxide ions. This would account for the increase in manganese(II) ion in the solution after the breaking of the circuit. (*B*) They may be oxidized to manganese(III) ions by the dioxide and may then diffuse into the interior of the oxide layer. In the early part of the discharge the diffusion process is the only one in operation on breaking the circuit.

At *p*H 5 an ammonium salt solution can react with manganese(III) oxyhydroxide or mixtures of this with dioxide to give manganese(II) ion in solution (5). The favorable effect of the higher hydrogen ion activity on this reaction is apparent from equation (I). Therefore, in a discharge at *p*H 5, manganese(II) ion appears in the solution soon after the beginning.

In addition to the discharges shown in Table I, three continuous discharges in 4M, 2M, and 1M ammonium chloride electrolytes, all of *p*H 7, gave totals of 0.054, 0.038, and 0.021 mmole of manganese(II) ion, respectively.

Ferrell and Vosburgh (3) assumed that the discharge reaction of electrodes of the type used in the present investigation takes place at the inner surface of the manganese dioxide, next to the graphite. Their theory is not dependent on this assumption, and it now seems much more probable that the reaction takes place on the outer surface, and the electrode potential is determined by the composition of the outer surface. The formation of manganese(II) ion is best understood if it is assumed that the reaction takes place at the surface exposed to the solution.

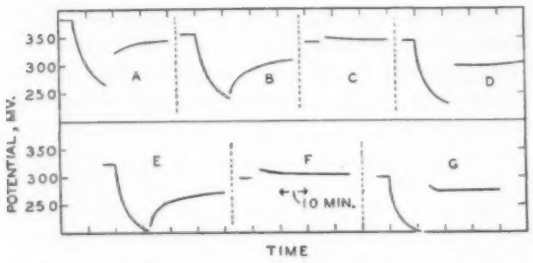

FIG. 2. Five successive 20 ma-min discharges followed by recovery periods, showing effect of pyrophosphate treatment immediately after discharge (A, D, and G) and on electrode at equilibrium (C and F); B and E are controls.

An experiment was undertaken to provide additional evidence on this point.

An electrode was discharged in 1M ammonium sulfate containing 0.01M ammonia, *p*H 7.0, against a lead anode in the usual way for about 20 ma-min at 1.6 ma. Then the circuit was broken, and the electrode was quickly transferred to a 1M ammonium sulfate solution containing sodium pyrophosphate at a concentration of 0.08M and having a *p*H of 7.0. It was kept in this solution 2 min while the solution was stirred mechanically at the same rate as during the discharge. After a quick washing with electrolyte, the electrode was replaced in the discharge vessel, and the record of its potential continued. The record of the discharge and recovery is shown in Fig. 2A. After complete recovery, a second discharge and recovery were carried out without the pyrophosphate treatment, as a control (Fig. 2B). It is evident from Fig. 2A and 2B that the pyrophosphate treatment after the first discharge accelerated the recovery from polarization. This behavior was probably the result of the extraction of some lower oxide from the electrode surface by the pyrophosphate. Following recovery from the second discharge, a pyrophosphate treatment similar to that following the first discharge was given (Fig. 2C). This delayed pyrophosphate treatment caused a small increase in potential followed by a decrease to a value slightly above the constant value preceding the treatment.

In two more 20 ma-min discharges on the same electrode the hastening of the recovery after a pyrophosphate treatment immediately following discharge was observed to an increasing extent (Fig. 2D and 2G). In the last discharge the potential immediately after pyrophosphate treatment was decreasing, followed later by an upturn in the recovery curve. The two treatments described above were separated by a 20 ma-min discharge followed by normal recovery and subsequent pyrophosphate treatment (Fig. 2E and 2F), the latter causing a somewhat larger temporary increase in potential than that of the previous delayed treatment.

The amount of manganese(II) and (III) ion that had dissolved in each of the pyrophosphate treatment solutions was determined and found to increase from the first to the third to the fifth solution, and to be present in much smaller and about equal amounts in the second and fourth solutions. A series of experiments similar to the above with a second electrode using ammonium chloride electrolyte gave comparable although less pronounced results, with practically no effect of the pyrophosphate treatment evident until the third in the series, comparable to Fig. 2D.

The use of pyrophosphate ion was based on its ability to form complex ions with manganese(II) and (III) ions. A brief treatment with pyrophosphate must extract lower oxide from the exterior surface. This causes an increase in electrode potential on an electrode which had previously been at equilibrium, when it contains sufficient lower oxide. When a freshly discharged electrode is treated with pyrophosphate, increase in potential and amount of manganese extracted is larger than for an electrode at equilibrium, indicating that there must be more lower oxide on the outside surface of the polarized electrode. The small decrease in potential following the last pyrophosphate treatment (Fig. 2G) is caused by the removal of sufficient lower oxide from the surface layer to make it richer in dioxide than the layer immediately beneath it, and diffusion of lower oxide at first takes place toward the outer layer.

A different experiment led to similar conclusions. An electrode was placed in 2M ammonium chloride electrolyte of *p*H 7.1 containing $10^{-3}N$ hydrogen peroxide. The solution was stirred, and the electrode potential was measured continuously. The potential dropped rapidly at first and then more slowly as in a normal discharge. After 37 min the electrode was quickly transferred to another vessel containing identical electrolyte but without hydrogen peroxide.

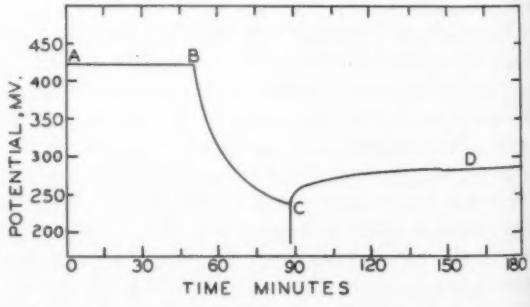

FIG. 3. A chemical discharge by the action of H_2O_2 in NH_4Cl electrolyte on MnO_2 electrode at 30°C. A-B, Electrode in 2M NH_4Cl, 0.01M NH_4OH, *p*H 7.11; B-C, electrode in 2M NH_4Cl, $10^{-3}N$ H_2O_2, *p*H 7.12; C-D, electrode in 2M NH_4Cl, 0.01M NH_4OH, *p*H 7.12.

The potential started to rise and followed a curve resembling that of recovery from polarization, as shown in Fig. 3. Since hydrogen peroxide in ammonium chloride solution reduces manganese dioxide, this experiment is in agreement with conclusions that the discharge reaction takes place at the exterior surface and that the electrode potential is determined by the composition of the exterior surface.

Acknowledgments

This work was carried out under Contract Nonr-1016(00) with the Office of Naval Research. The authors are indebted to Mr. John S. Reiser for a number of preliminary experiments.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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Nature of the Passive Film on Iron in Concentrated Nitric Acid[1]

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ABSTRACT

The film responsible for passivity when iron is immersed in concentrated nitric acid is shown to be ferric acid or a related higher valence iron compound. This was proved (*a*) by demonstrating formation of chromates when a 2.84% Cr-Fe alloy is passivated, (*b*) by showing complete suppression of the iron-nitric acid reaction when iron is previously immersed in potassium ferrate solution, and (*c*) by immersing passive iron in NaOH solution and observing higher valence iron compounds displaced from the surface by adsorbed OH^-. The maximum of 2×10^{-8} mole ferric acid/cm² that was found is the same order of magnitude as moles chromate adsorbed on iron from chromate solutions as reported by other investigators. This amount of ferric acid, when it decomposes, is calculated to form a film of ferric oxide 40–125 Å thick, which thickness range agrees with that of residual oxide films on passive iron measured previously by others.

The higher valence iron compound forms at anodic areas of the iron surface during the iron-nitric acid reaction. When sufficient local concentration is achieved, the compound adsorbs (chemisorbs) on iron, satisfies metal surface affinities, and is itself stabilized against decomposition by adsorption. The metastable compound breaks down by cathodic reduction, mechanical shock, or presence of halide ions, the latter either displacing the adsorbed compound or hastening its decomposition. The roles of urea and hydrogen peroxide in nitric acid are discussed.

Introduction

In a previous paper (1), several experiments on passivation of evaporated iron films established that a certain amount of iron reacts rapidly with concentrated HNO_3 before the reaction is retarded. Preexposure of the iron films to oxygen, carbon monoxide, or dilute potassium dichromate solution appreciably reduced the initial amount of iron reacting. This was explained in terms of local action currents on the iron surface serving to polarize anodic areas. The above substances adsorbed on iron increase the effective cathodic area, thereby increasing the anodic current density. It was observed, correspondingly, that external anodic polarization of iron in nitric acid decreased the amount of iron reacting before passivation. Continued investigation along similar lines is reported herewith. These results, combined with important contributions to the subject by Bonhoeffer and co-workers (2), provide a clearer interpretation of the passivation mechanism by nitric acid than has been available heretofore. The process apparently is not so simple as the formation of a barrier film of ferric oxide.

[1] Manuscript received January 31, 1955. This paper was prepared for delivery before the Boston Meeting, October 3 to 7, 1954.

[2] Present address: American Cyanamid Company, Piney River, Virginia.

Experimental Procedure

Experimental techniques were essentially the same as those employed by Gatos (1). Two types of iron surfaces were utilized; in one case by evaporation of iron onto glass, and in the other by employing Armco iron foil. Evaporated films were prepared by heating in vacuum either pure iron wires of 0.040-in. diameter, or by wrapping iron wire on electrically heated tungsten filaments of 0.025-in. diameter. The iron vapor was condensed on slowly rotating glass cylinders 35 mm long and 4 mm in diameter. The coated cylinders were then removed magnetically from the evaporation chamber and sealed off in glass tubes, or, when surface area determinations were made, the cylinders were transferred to another portion of the vacuum system through glass tube conduits without exposure to air.

Absolute surface area measurements were made on a number of such films by the B.E.T. method (3) in which ethane was adsorbed on the metal at liquid oxygen temperatures (−183°C). Use of ethane permitted surface area measurements on specimens having as little as 100 cm² of absolute surface. It was found that relatively smooth films, of roughness factor 1.7, were obtained from iron-wrapped tungsten wires, whereas films of greater absolute surface were formed by evaporation from iron filaments (roughness factor = 5–11). Apparently, the lower deposi-

TABLE I. *Effect of source of iron, N_2 and O_2 exposure, and absolute surface area on amount of iron reacting with HNO_3. Sp gr 1.43*

Area of evaporated iron film on glass = approx. 4.2 cm²

Source of iron	No. of films tested	Original film thickness* Å	Exposure of film before reaction	Mg Fe reacted per cm² geometric area
National Bureau of Standards	10	1700–2680	Vacuum	0.092 ± 0.019
Westinghouse (Puron)	13	2320–3400	Vacuum	0.095 ± 0.013
Mallinckrodt	5	2350–2400	Vacuum	0.090 ± 0.006
Westinghouse (Puron)	5	1980–4330 (Roughness factor = 8.7–10.8)†	Vacuum	0.108 ± 0.012
Westinghouse (Puron)	9	1940–2500	1 atm O_2, 30 min	0.040 ± 0.008
Westinghouse (Puron)	8	Approx. 2000	1 atm O_2, 30 min subsequent evacuation	0.043 ± 0.011
Westinghouse (Puron)	6	Approx. 2000	1 atm N_2 for <1 min	0.091 ± 0.019

* Based on total amount of evaporated iron (density = 7.86), and geometric area.

† Roughness factor for other films listed in this table is approximately 1.7.

tion temperatures using iron filaments retarded sintering of the condensed film, resulting in an irregular array of crystals and perhaps a porous structure. These films of higher roughness factors were used only in comparison experiments, the majority of the data being obtained with the smoother films. Little difference in reacted iron was found on passivating the rough or smooth films (Table I).

The Armco foil specimens were generally 3 x 3 cm and 0.0075 cm thick. After preliminary degreasing in boiling benzene, they were pickled for 2 min in 15% HCl at 100°C (210°F), washed, and immersed successively in boiling acetone and boiling benzene. Specimens before use were aged in a desiccator overnight; reproducibility was thereby improved probably by allowing escape of interstitial hydrogen absorbed during the pickling operation.

It was necessary to bring the iron-coated glass cylinders into contact with concentrated nitric acid without contamination by exposure to the atmosphere. This was done by inscribing a circumferential scratch on the glass tube in which the iron-coated cylinder was contained, and placing the tube in an H-shaped glass holder of proper dimensions at the bottom of a beaker of concentrated nitric acid. Using a glass rod, sufficient pressure was applied to break the tube and bring the acid into rapid contact with the iron film. In some experiments, the evacuated specimen tube was broken inside a nitrogen-filled test box fitted with rubber gloves, and the specimen quickly immersed in nitric acid. Films exposed a short time to nitrogen behaved the same as those retained in vacuum.

Nitric acid was purified by distillation in an all-Pyrex still to remove small but annoying traces of iron. Immediately before use, the distilled acid was freed of dissolved oxides of nitrogen by bubbling through gaseous nitrogen for one or more hours. This operation was necessary because of the significant effect of nitrogen oxides on the passivation reaction. The specific gravity of the distilled acid was 1.43 ± 0.005 at 15.6°C (60°F).

The amount of iron reacting with nitric acid previous to passivation[3] was analyzed colorimetrically using the orthophenanthroline method. Nitric acid solutions were evaporated to dryness, the residues taken up in 1:1 HCl, and iron determined using an electrophotometer according to the method described by Sandell (4). This method was considered an improvement over the KSCN colorimetric method used by Gatos.

Chromium, in the hexavalent state, was determined colorimetrically using di-phenylcarbazide. The method was essentially that described by Sandell (5), except that nitric acid was used instead of sulfuric acid to provide the required acidity for development of a violet color. Total chromium was obtained by the same method after oxidation of Cr^{3+} to Cr^{6+} with hydrogen peroxide in dilute alkali. For both iron and chromium analyses, appropriate standards were prepared in solutions of the same kind as those common to the passivation experiments.

Effect of Oxygen Pre-exposure

Exposure of evaporated iron films to oxygen for 30 min or longer was found previously to reduce, by approximately one half, the amount of iron reacting with nitric acid before passivity was established. This was confirmed by the present series of experiments (Table I). The next step was to determine minimum partial pressure of oxygen at which the effect is observed. Evaporated films of iron on glass cylinders were allowed to remain in the glass evaporation system, and were then exposed to oxygen at various pressures for a total of ½ hr. Adjustment of

[3] Time of immersion, 2 min, was not critical.

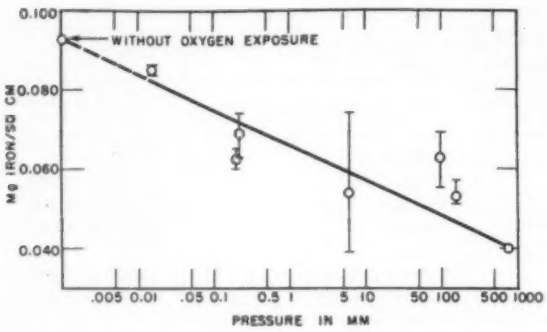

FIG. 1. Amount of iron reacting in nitric acid after exposure to oxygen at various pressures for ½ hr.

pressure to the required value necessitated an additional preliminary time of 15–30 min. After exposure, specimens were sealed off in glass tubes and immersed directly in nitric acid by breaking the container under acid as described previously. Analyses for iron as a function of the oxygen pressure to which the films were exposed are plotted in Fig. 1. There is a gradual trend from the maximum amount of reacted iron for films retained in vacuum, to about one half this value for films exposed to 1 atm O_2. The scatter of data is typical of passivation phenomena, and is not unexpected. No critical pressure of oxygen was found, but instead a trend toward lesser amounts of iron reacting as the pressure of oxygen was increased.

Further tests showed that the effect of oxygen at 1 atm can also be achieved at lower pressures if time of exposure is prolonged. Three films exposed to 2.7×10^{-4} mm oxygen for 24 hr and then reacted with nitric acid in the usual way gave values of 0.055, 0.054, and 0.067 (average 0.058) mg Fe/cm², which can be compared with the value of 0.040 mg Fe/cm² after exposure to 1 atm O_2 for 30 min. Two films sealed off after six hours' exposure at 4×10^{-3} mm O_2 pressure produced 0.047 and 0.059 (average 0.053) mg Fe/cm². Oxygen apparently chemisorbs on iron more rapidly the higher the external pressure. Hackerman and Antes (6) came to the same conclusion through Volta potential measurements of iron films exposed to oxygen at various pressures. It is also possible that rate of oxidation of iron to iron oxide increases with O_2 pressure. However, Tammann and Köster (7) reported that partial pressure of oxygen has no effect on oxidation rate of iron at 331°C where thin films are formed, and, hence, an effect of pressure instead on rate of chemisorption is favored.

Effect of Subsequent Evacuation

After exposure of several films to 1 atm of oxygen for ½ hr, the system was evacuated to 10^{-6} mm pressure for periods ranging from 4 to 12 hr. These films on immersion in nitric acid reacted to the same extent as did those not subject to evacuation after exposure to oxygen. In other words, effects of oxygen exposure were not removed by evacuation. Data for eight different films gave an average value of 0.043 ± 0.011 mg Fe/cm² (Table I), which compares with the average value for nine films, exposed similarly to oxygen but not evacuated, of 0.040 ± 0.008 mg Fe/cm². These measurements can be taken as evidence that effects of oxygen at 1 atm after 30-min contact with iron cannot be removed from the surface by subsequent lowering of the pressure.

Independent measurements of oxygen adsorption on iron films confirmed that the gas is irreversibly adsorbed. These measurements, to be reported in detail elsewhere, showed that adsorption of oxygen proceeds at a high rate initially, followed by a slow rate after a certain amount of oxygen covers the surface. Several iron films were exposed to oxygen at a final pressure of 1.8 to 7×10^{-3} mm Hg pressure for 1–5 hr, and were then evacuated at less than 10^{-6} mm Hg pressure for 5–12 hr. Oxygen was then allowed to adsorb on the surface again, but the observed rate of adsorption was always low and not characteristic of the high initial rate for a clean iron surface. Failure to regenerate the initial high rate of adsorption is proof that the original surface of iron is not regained by evacuation. A further check was made by adsorbing 17.4 cc-mm (9.4×10^{-7} mole) oxygen at a final pressure of 3.6×10^{-3} mm, and allowing the gas (17 ml) in contact with 167 cm² iron (absolute surface) to expand into a known volume (428 ml). The calculated final pressure (0.14×10^{-3} mm), assuming no release of previously adsorbed gas on iron, checked the observed pressure (0.13×10^{-3} mm). Armbruster and Austin (8) also reported that oxygen is irreversibly adsorbed on iron at room temperature.

The foregoing effects of evacuation on passivity differ from the previous observations by Gatos and Uhlig who reported that the effects of oxygen exposure were removable by pumping out the system. Detailed scrutiny and careful examination of all the facts revealed no certain reason for the discrepancy, but it is possible that the method they used to introduce oxygen-exposed specimens into the acid was at fault. This was done by heating one end of the glass tube and plunging it into acid, whereupon the tube fractured by thermal shock. If in so doing the iron films were heated unintentionally, the effect of oxygen would have been erased as Freundlich and coworkers showed (9), and with whose results present experiments are now in accord. Heating converts adsorbed oxygen to iron oxide (or, alternatively, the iron oxide film is sintered) which is not as effective a cathode as the adsorbed gas (or the initial oxide)

and, hence, larger amounts of iron dissolve subsequently in the passivation reaction.

Present results otherwise are in qualitative agreement with those reported earlier, including the indifferent effect of pre-exposure to nitrogen (Table I). Quantitatively, the amounts of iron reported per unit area for the present experiments are roughly one half those reported by Gatos and Uhlig. The differences were not found to be caused by variation of true surface area or source of iron, as summarized data of Table I show. The main factor appeared to be the present adoption of an improved method of analysis for small amounts of iron. This method required evaporation of numerous nitric acid solutions to dryness, hence was tedious and extremely corrosive to adjacent equipment. Nevertheless, the accuracy of results was much better than omitting evaporation, both because the concentrated acid no longer interfered with the color reaction, and because the possible size of sample for analysis was inherently larger. It is felt, therefore, that the present values for iron are more nearly correct.

Additions to Nitric Acid

Gatos (1) reported that exposure of iron films to oxygen-saturated 0.1% $K_2Cr_2O_7$ reduced the amount of iron reacting with concentrated nitric acid as time of exposure increased, with very little or no iron reacting for exposures greater than 30 min. This was confirmed by the present series of experiments using two evaporated iron films, three hydrogen-reduced Armco foil specimens, and four pickled Armco foil specimens. Each was pre-exposed 45 min to 0.1% $K_2Cr_2O_7$, and the excess solution drained off on filter paper before immediate immersion into nitric acid. For all specimens, the weight loss on passivation was 0.000 ± 0.001 mg/cm². In other words, pre-exposure of iron to dilute chromate solutions completely passivates it with respect to reaction with concentrated nitric acid.

Addition of potassium dichromate directly to nitric acid was found to accomplish the same thing, although the concentration required was higher than 0.1%. Armco foil specimens were used, previously pickled in 15% HCl at 100°C for 2 min, and allowed to age in a desiccator overnight. Data are plotted in Fig. 2. There is no effect on the reaction by dissolved chromate up to 0.1 g/50 ml acid (2 g $K_2Cr_2O_7$/liter). The higher value for reacted iron using Armco foil (0.07 mg/cm²) than for evaporated films (0.04 mg/cm²) has an uncertain origin; it may be caused by interstitial hydrogen, impurities in the metal surface, or, more likely, edge effects and specimen shape, since convection currents and stirring, for example, are known to affect the passivation reaction. A rather sudden reduction in reaction rate occurs between 0.1

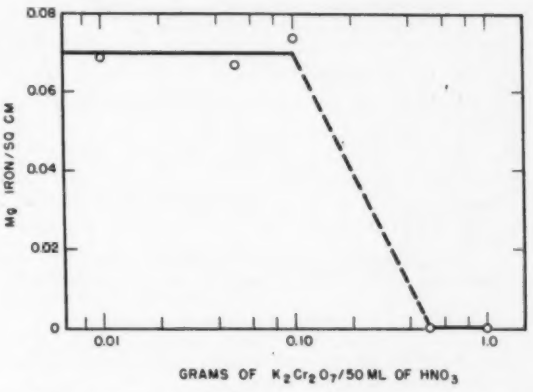

FIG. 2. Effect of addition of $K_2Cr_2O_7$ to nitric acid (sp gr 1.43) on amount of iron reacting.

and 0.5 g $K_2Cr_2O_7$/50 ml nitric acid (2 to 10 g $K_2Cr_2O_7$/liter), and the rate remains essentially zero for higher concentrations. The data indicate, therefore, that the passivating effect of chromates can be induced either by pre-exposure of iron to dilute solutions of chromates for a sufficient time, or by adding chromates directly to the nitric acid.

Similar experiments were carried out with addition of potassium nitrite to the acid (Fig. 3). Liberation of nitrous acid has an appreciable effect on the amount of iron reacting when the KNO_2 concentration is over 0.1 g/50 ml HNO_3 (2 g/l). Below this concentration, the effects are erratic, with either the usual amount of iron reacting, as when nitrites are absent, or almost none reacting as is uniformly true of concentrations over 0.1 g KNO_2/50 ml acid. It is important to note, from the standpoint of mechanism discussed later, that the average amount of iron reacting in acid containing more than the critical amount of dichromate or nitrite was essentially 0.000 mg Fe/cm² for dichromate (5 determinations), but measurably higher for nitrite, namely 0.0013 mg Fe/cm² (8 determinations).

The obvious importance of nitrous acid or its de-

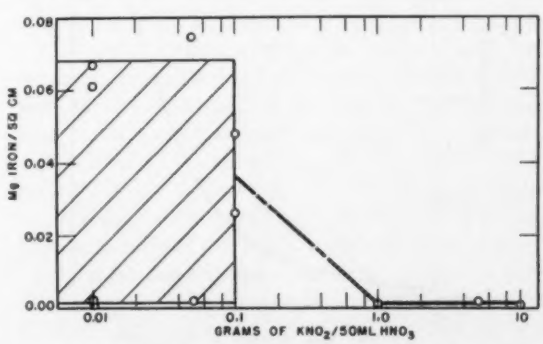

FIG. 3. Effect of addition of KNO_2 to nitric acid (sp gr 1.43) on amount of iron reacting.

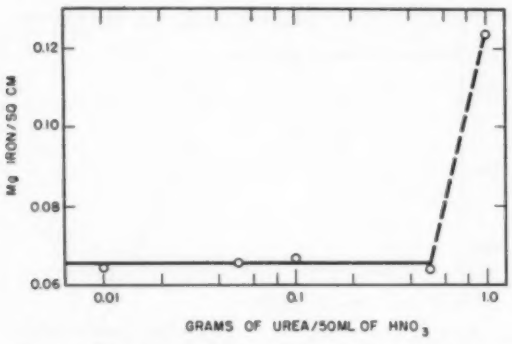

FIG. 4. Effect of addition of urea to nitric acid (sp gr 1.43) on amount of iron reacting.

composition products to the passivation reaction suggested adding substances capable of reaction with HNO_2 and which reduce its concentration. Urea is one such substance, which is stated (10) to react as follows:

$$2HNO_2 + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + 3H_2O$$

The reaction products have also been stated to include cyanic acid, HCNO.

According to Vetter (11), an excess of urea reduces the ultimate concentration of nitrous acid in nitric acid to about 1×10^{-5} mole/liter. Fig. 4 shows that below 0.5 g urea/50 ml HNO_3, iron was passivated with approximately the usual amount of iron reacting. Even with as little as 0.01 g urea, however, no color developed in the acid, and considerable gas was evolved, showing that urea was effective in removing the nitrous acid. At the highest concentration or 1.0 g urea/50 ml, HNO_3, which approached the solubility of urea in the acid, approximately twice as much iron reacted as for smaller concentrations. In the latter solution, however, iron was passive only temporarily, with periods of passivity alternating with periods of activity. Naturally, more iron reacts under these conditions than when passivity is stable over the usual 2-min period of immersion in the acid.

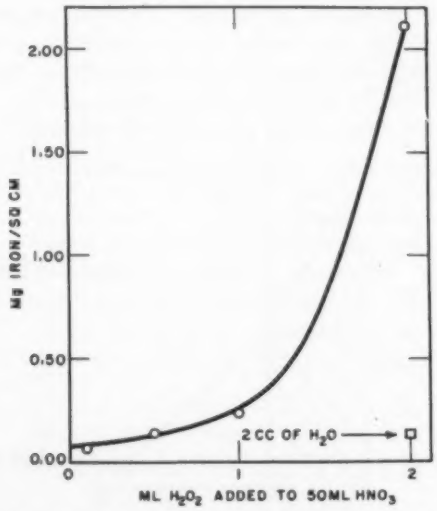

FIG. 5. Effect of addition of 30% hydrogen peroxide on the amount of Fe reacting in nitric acid (sp gr 1.43).

Addition of hydrogen peroxide showed a more marked effect on the amount of iron reacting. Data are plotted in Fig. 5, each point representing an average of two determinations. As in the case of urea, the effect was accompanied by periodic breakdown and re-formation of the passive state, each cycle being attended by dissolution of iron. The higher the concentration of H_2O_2, the more rapid was the frequency of breakdown. The effect observed is not one of dilution, because addition of water equivalent to that added with hydrogen peroxide showed only a small effect (Fig. 5).

Formation of Higher Valence Compound

The facts thus far provided evidence that $K_2Cr_2O_7$ either on the surface of iron or in nitric acid substantially reduces attack of iron during the passivation reaction. Potassium nitrite added to nitric acid also reduces the attack, with an effect slightly less than for dichromate. Further experiments showed that pre-exposure of iron to saturated nitrite solution for 1 hr followed by washing in water had no measurable effect on the amount of iron reacting with nitric acid, contrary to similar pre-exposure to dichromate. Potential measurements in distilled water of iron wires (0.040-in. diameter, sealed in lead glass) previously passivated either in concentrated HNO_3 or in 0.1% K_2FeO_4 and washed in water, were of the same order initially, namely 0.9–1.0 v on the normal hydrogen scale. It seemed reasonable, therefore, to hypothesize the formation of a compound during the iron-nitric acid reaction similar in structure and properties to ferric acid, H_2FeO_4, as the key substance responsible for passivity. Any of the normal oxides of iron cannot account for the observed noble potential, as Bonhoeffer (2) showed. Although ferric acid is unstable when dissolved in acids, its decomposition rate is probably retarded when it is adsorbed on iron.

To check the role of ferric acid, potassium ferrate was prepared, in accord with a method described by Thompson, Ockerman, and Schreyer (12). Exposure of Armco iron specimens to freshly dissolved 0.1% solution[4] for 45 min, draining of excess ferrate solution onto filter paper, and immersion of the specimen into nitric acid in the usual way showed indeed that iron was protected from reaction with nitric acid in

[4] The solution decomposed slowly, but the purple color of ferrate was still visible at the end of 1 hr.

the same manner as was provided by pre-exposure to dichromate solutions. A small amount of iron was found in nitric acid after immersion (0.003 and 0.002 mg Fe/cm² in two experiments), which is accounted for by residual ferrate solution adhering to the iron surface. It was not possible, of course, to check the effect of ferrate added directly to nitric acid as was done with chromate because of the instability of the compound in acid solutions.

The next experiments were directed toward detection of hexavalent iron compounds possibly formed in the passivation reaction. The transient nature of such compounds and their obviously small concentration at any time during the reaction made the task difficult. However, since chromates are relatively stable, and conditions for their formation are reasonably parallel to those for hexavalent iron compounds, it was decided to use a small amount of alloyed chromium in iron as a tracer element. Accordingly, specimens of a laboratory-prepared melt of 2.84% Cr-Fe alloy were fabricated into sheet specimens each having a total geometric area of about 6 cm². This alloy, immersed in concentrated nitric acid for 2 min, lost 0.025 mg/cm², which is about one third the value, 0.07 mg/cm², for pure iron. (Higher chromium alloys corroded still less.)

Because iron interfered to some extent with analyses for chromium using the di-phenyl carbazide color reaction, the solution was made alkaline to *p*H 8, and the ferric hydroxide centrifuged off. A calibration curve was constructed using weighed amounts of $K_2Cr_2O_7$ in concentrated HNO_3. Total chromium, when required, was determined by first oxidizing Cr^{3+} to Cr^{6+} in dilute alkali using H_2O_2.

The first experiments involved successively passivating the 2.8% Cr-Fe alloy for a total of 100 times in 50 ml of concentrated HNO_3, activating the specimen each time in dilute HCl followed by thorough washing in distilled water. Large amounts of oxides of nitrogen were generated in the nitric acid, and the passivating reaction each time was characterized by a dark reddish-brown film creeping over the alloy surface. Careful analysis of the acid revealed complete absence of hexavalent chromium, with the analytical method estimated to be sensitive to about 50 μg of dichromate. The test was repeated using cathodic activation of the specimen in water so as to avoid possibility of contamination by chloride ion, but with the same result.

The next experiment was the anodic polarization of the alloy specimen (5.6 cm²) in 3% Na_2SO_4 for 1 hr at a current density of 40 ma/cm². Oxygen was evolved over all the surface of the anode indicating that the alloy was passive, and slight precipitation of ferric hydroxide within the solution revealed some metal dissolution in addition. The anodic corrosion accounted for 1% of the total electricity passing through the cell. In this instance chromate was found, and, furthermore, all the chromium going into solution was hexavalent. Data for this and the following few experiments are summarized in Table II.

TABLE II. *Analysis of corrosion products of passivated 2.8%* Cr-Fe *alloy*

Passivation treatment	Total metal in solution		Cr_2O_7 found	Current efficiency for $Fe \rightarrow Fe^{+++} + 3e^-$
	Cr	Fe		
	mg	*mg*	*mg*	%
1. HNO_3 100×, HCl activation	1.30	—	0.0	—
2. HNO_3 50×, cathodic activation	0.63	29.2	0.0	—
3. Anodic polarization 3% Na_2SO_4, 40 ma/cm², 1 hr	0.046	1.6	0.095	1
4. Anodic polarization, HNO_3, 40 ma/cm², 1 hr	2.4	98.7	0.0	63
5. Anodic polarization, HNO_3, 40 ma/cm², ½ hr, H cell	1.5	57.0	1.6	67
6. Same as 4, HNO_3 saturated with urea, ½ hr:				
(*a*) Analysis for Cr^{6+} immediately	1.21	53.0	0.36	63
(*b*) Analysis for Cr^{6+} 2½ hr after electrolysis	—	—	0.25	—
(*c*) Analysis for Cr^{6+} 12 hr after electrolysis	—	—	0.0	—
7. HNO_3 saturated with urea, 50×, cathodic activation	0.62	—	0.0	—

The fourth experiment consisted of anodically polarizing the alloy in concentrated nitric acid, again for 1 hr at 40 ma/cm². There was more anodic corrosion than before, about 63% of the current representing anodic dissolution compared with 1% for Na_2SO_4. However, no dichromate was detected.

The difference in results, depending on electrolyte, suggested that hexavalent chromium in nitric acid was probably being reduced by cathodic reduction products freely circulating throughout the volume of acid. In Na_2SO_4, the cathodic products are H_2 and NaOH, the hydrogen escaping from the solution, but in nitric acid, products such as nitrous acid remain in solution. It was found, in accord with this reasoning, that small quantities of potassium nitrite added to concentrated HNO_3 containing dissolved $K_2Cr_2O_7$ completely reduced the dichromate, as determined by analysis. In other words, dichromate rapidly oxidizes nitrous acid (Table III).

The fifth experiment, therefore, was to repeat the foregoing experiment, but with separation of anolyte and catholyte in an H-type cell with a fritted glass disk separating the two compartments. In addition, a stream of nitrogen was passed through

TABLE III. *Reduction of* $K_2Cr_2O_7$ *in concentrated* HNO_3 *by additions of* KNO_2

g KNO_2 added to 50 ml HNO_3 + 0.41 ppm $Cr_2O_7^{--}$	ppm $Cr_2O_7^{--}$ found by analysis
0.10	0.0
0.05	0.0
0.01	0.0
0.0	0.42
0.0	0.39

both compartments to remove any oxides of nitrogen from solution.

Using this arrangement with a current density of 40 ma/cm² for 30 min (area anode = 6.1 cm²), analysis of the anolyte now revealed positive presence of dichromates, with a current efficiency for anodic dissolution remaining at about 60–70%. In absence of reducing agents, therefore, hexavalent chromium is formed on anodic polarization of the 2.8% Cr-Fe alloy in nitric acid.

The sixth experiment involved the addition of urea to concentrated nitric acid which, as noted previously, reacts with nitrous acid and greatly reduces its concentration. Using the electrolytic cell without separation of anolyte and catholyte, dichromates this time were found. The amount of dichromate decreased with time after electrolysis was discontinued, as data of Table II show, probably because urea is oxidized slowly by dichromates. This, plus the fact that some nitrous acid is present, also explains the smaller quantity of Cr_2O_7 found compared with experiment 5. However, in absence of anodic polarization, and by merely dipping the specimen 50 times into the urea-nitric acid mixture, activating the specimen cathodically in water each time, no dichromate was found (experiment 7, Table II). Apparently, the dichromate under these conditions is reduced by HNO_2, formed in close proximity to the anodes, more rapidly than urea can diffuse to the metal surface and react with HNO_3. Vetter (11) has shown, for example, that it requires approximately 1 min for a 1% solution of urea in concentrated HNO_3 to reduce the nitrite concentration from 4×10^{-3} to 1×10^{-4} mole/liter.

Detection of Hexavalent Chromium Compound

With definite formation of dichromates on anodic polarization of the Cr-Fe alloy in nitric acid, the next question concerned the analogous formation of a hexavalent iron compound and its similar properites as a passivator. This question previously had been answered in part by pre-exposing iron to dilute potassium ferrate or to potassium chromate, and observing in either instance the complete suppression of reaction with nitric acid.

Evidence from the potential behavior of iron in various chromate solutions indicated that the Langmuir adsorption isotherm is obeyed (13), confirming that passivation by chromates is accompanied by their adsorption on iron, as had been suggested earlier (14). Radioactive tracer studies (15) on the amount of radioactive chromium on the surface of iron as a function of chromate concentration also showed that an approximate adsorption isotherm is followed. Evidence for adsorption accompanying passivation was also reported by Powers and Hackerman (16). They showed that chromates were adsorbed on iron below *p*H 11 and could not be washed off (chemisorption), whereas above *p*H 11 chromates were not adsorbed at all. These facts immediately suggested that hexavalent iron compounds analogously may adsorb on iron. Furthermore, if they are the cause of passivity in nitric acid, they should be released from the metal surface by immersing passive iron in strong alkalies, and, in the case of iron containing alloyed chromium as tracer, some chromates should be released simultaneously.

The next experiment, therefore, was to passivate the 2.84% Cr-Fe alloy (6.1 cm² area) in concentrated HNO_3, wash in water, immerse in 2*N* NaOH, then in dilute HCl, and again wash in distilled H_2O, repeating this procedure successively 50 times. Analysis of the sodium hydroxide solution, carrying out this procedure, showed indeed the presence of 53 μg of Na_2CrO_4. Repetition of the same procedure using HCl instead of HNO_3 did not passivate iron and, correspondingly, produced no detectable amount of chromate. This experiment proved, therefore, that hexavalent chromium forms when the chromium-iron alloy is passivated in concentrated nitric acid, and furnishes strong evidence that the chromates so formed are in part chemisorbed.

Formation of Hexavalent Iron Compounds in Nitric Acid

With the preceding evidence for hexavalent chromium, a cell was set up to demonstrate the possibility that hexavalent iron can form by the nitric acid-iron reaction. To one compartment of an H-type cell, 5*N* NaOH was added in contact with an Armco iron electrode (2 x 2 cm), and concentrated HNO_3 was added to the other compartment in contact with a platinum electrode of similar size. On electrically short circuiting the two electrodes, light purple reaction products, characteristic of sodium ferrate and exhibiting typical oxidation reactions, streamed off the iron, accompanied by oxygen evolution. A similar experiment was repeated using 0.1*N* NaOH instead of the more concentrated alkali with identical although less pronounced results. By employing 3% Na_2SO_4 instead of NaOH, however, no ferrate formed visibly, oxygen being the only ob-

servable anodic product. In a solution such as this, it is probable that if ferrate is formed, it is immediately adsorbed on the electrode surface with no tendency for its release, whereas in NaOH the hydroxyl ion adsorbs preferably and continuously displaces ferrate ions.

It remained to demonstrate that the compound formed on pure iron and displaced by hydroxyl ions has oxidizing properties typical of ferrates. Analysis of the suspected compound was based on a method described by Schreyer, Thompson, and Ockerman (17). To 20 ml saturated NaOH, 1 ml of chromic chloride solution (1.7 g $CrCl_3$/100 ml) and 5 ml H_2O were added. Any ferrate introduced into this solution reacts with Cr^{3+} to form chromate in accord with:

$$2FeO_4^{--} + 2Cr^{3+} \rightarrow 2CrO_4^{--} + 2Fe^{3+}$$

The corresponding chromate was analyzed by diluting the solution to 50 ml, taking a 10 ml aliquot, diluting this to 15 ml and carefully adding H_2SO_4 to *p*H 8 or 9. Ferric hydroxide was centrifuged off, and the solution then acidified with 2 ml of 5*N* H_2SO_4. On dilution to 40 ml, 2 ml of di-phenyl carbazide reagent were added, dilution carried to 50 ml, and the violet color as developed by dichromate was compared with suitable standards using the electrophotometer.

A coiled Armco iron specimen of 60 cm² area, suspended from a glass hook, was passivated in concentrated nitric acid, and carefully washed in one or more beakers of distilled water without destroying passivity. The coil was then plunged into the above-described NaOH solution containing Cr^{3+} and allowed to remain about 10 min, after which analysis of the alkaline solution was carried out for CrO_4^{--}. Blank determinations using the identical procedure were run with platinum sheet having the same area as iron. Chromates were found over and above small blank corrections, indicating that ferrate or an analogous compound is formed when iron reacts with concentrated nitric acid. A summary of results is given in Table IV. The data show that reproducibility, typical of most experiments in passivity, was not good, but nevertheless was adequate to prove the point. The amount of ferrate corresponding to the analyzed chromate appeared to be independent of whether one or three washes were employed, which may be taken as further evidence that the compound is chemisorbed on iron.

The variable amounts of ferrate may indicate partial decomposition taking place during washing and at the time of immersing the iron specimen into NaOH. Some specimens may have lost most of their passivity, judging by the amount of ferrate found and that produced by a specimen known to be

TABLE IV. *Analyses of passive film on iron for ferrates and iron content*

No. of washes in water	μg CrO_4^{--} formed on immersion in NaOH + Cr^{+++} solution*	μg Fe in NaOH + Cr^{+++} solution†	Equivalent micromoles/cm²	
			FeO_4^{--}	Fe
1	138	1750	0.020	0.52
1	31	1310	0.005	0.39
1	57	1230	0.008	0.37
1	82	1580	0.012	0.47
2	89	1100	0.013	0.33
2	125	780	0.018	0.23
3	34	360	0.005	0.11
3	109	490	0.016	0.15
3	20	—	0.003	—
3‡	10	80	0.001	0.02

* Corrected for blank equal to 24 μg CrO_4^{--}.

† Corrected for blank equal to 120 μg Fe.

‡ Passivity intentionally destroyed by striking specimen on side of beaker in second wash.

active. Any nitrate or nitrite carried over on the passive iron surface could not have oxidized Cr^{3+} to CrO_4^{--}, because a check run showed that 100 mg KNO_3 or KNO_2 added to the NaOH solution containing Cr^{3+} did not produce chromate in excess of the normal blank. Moles of iron far in excess of moles of ferrate originated probably through carry-over of ferric nitrate and by corrosion of the iron specimen by an adhering film of acid not easily removed by washing. Data of Table IV show that additional water washes removed more of the residual acid solution, and thereby also reduced the amount of iron in the NaOH wash. It is questionable whether all the adhering solution can be removed without destroying passivity. Because of these factors, a more precise analysis of the surface compound responsible for passivity was not attempted.

Discussion

The experimental evidence can be interpreted, accordingly, in terms of a hexavalent iron compound, related to or identical with ferric acid, H_2FeO_4, which forms at the anode areas as a result of intense local action galvanic currents when iron reacts with concentrated nitric acid. The compound in part appears to be chemisorbed on the metal surface simultaneous with its formation. According to Bonhoeffer (2) and Vetter (18), local action currents increase with accumulation of nitric acid reduction products, in particular HNO_2, which act as cathodic depolarizers, the anodic current density eventually reaching the critical value for anodic passivation. Franck's (19) measurements of anodic passivation of iron in dilute H_2SO_4 showed that the critical value may be about 17 amp/cm². Anodic polarization of this magnitude suffices to produce ferrate or its analog either in situ, or in high concentrations at anodic

regions. The compound upon chemisorbing on iron is more stable chemically than in the free state. Chemical stabilization of the passive film by adsorption was suggested earlier by Bennett and Burnham (20) and by Bancroft and Porter (21) who considered that adsorbed metastable FeO_3 was responsible for passivity.

The chemisorbed compound, according to present authors' viewpoint, satisfies surface affinities of iron, and thereby reduces tendency of the metal surface to react, making it passive in the same sense as chromates are thought to cause passivity when chemisorbed on iron (13, 14, 22–24), or oxygen when chemisorbed on the stainless steels (13, 22–25).

In this connection, it may be significant that the maximum amount of ferrate released from passive iron is approximately 2×10^{-8} mole/cm² of geometric surface (Table IV). Geary (26) found a comparable amount of chromate to adsorb on oxide-free iron from 0.001M chromate solution, namely 5×10^{-8} mole/cm² geometric surface. Powers and Hackerman's (16) data for air-exposed iron correspond to 0.9×10^{-8} mole/cm², as do data of Brasher and Stove (15).

No iron reacts with nitric acid if iron is pre-exposed to ferrates or to chromates, because the surface is already covered with a passive film of the same kind as forms by reaction of acid with iron. At the same time, ferrate or its analog adsorbed on iron no longer has the same affinity for its external environment because of chemical attachment to the metal lattice underneath, and it is, therefore, relatively more stable with respect to acids, hydrogen peroxide, nitrous acid, and other reagents with which it normally reacts when in the free state.

High anodic local action current densities necessary for passivation are favored by adsorbed oxygen on iron, both because oxygen forms effective cathodic surfaces, and because local action currents are confined to smaller exposed anodic areas. Hence, less iron reacts with HNO_3 if the iron is pre-exposed to air. Pre-exposure to carbon monoxide similarly aids passivation through increased cathodic surface of adsorbed CO, similar to the behavior of adsorbed oxygen. At such time as the hexavalent iron compound forms an adsorbed layer or layers, the compound thereafter is continuously renewed at incipient small anode areas by continuing local action currents. The measured corrosion rate of passive iron in unstirred concentrated HNO_3 after several hours' immersion was found equal to about 20 mdd, which is equivalent to a total corrosion current ($Fe \rightarrow Fe^{+++} + 3e$) of 12 μamp/cm². At exposed anodes, of course, the current density is much higher. If 17 amp/cm² is necessary to achieve passivity, as Franck indicated, the ratio of anode to cathode area is $12 \times 10^{-6}/17$ or 7×10^{-7}. Vetter (11), using corrosion rates of iron in stirred concentrated HNO_3 containing 2% urea, similarly calculated the ratio to be 30×10^{-7}. Both values indicate that practically all the surface is cathode, a very small portion of which at any moment acts as anode.

Repair of the adsorbed film of compound occurs even in relatively dilute nitric acid. The lower conductivity and limited oxidizing properties of the dilute acid, together with a correspondingly large anodic area of iron when first immersed, are not sufficient to induce passivity. But when passivity is previously induced by immersion of iron into concentrated HNO_3, corrosion currents in dilute acid are entirely adequate for maintaining passivity.

So long as the compound remains on the surface and is repaired by local action currents, the specimen remains passive. Of course, if the metastable compound is broken down over more than a small region by mechanical action or heat, ensuing galvanic action of the induced anode in contact with a large area of cathode differing in potential by as much as 0.9 v (the potential difference between passive and active iron in water) is sufficient to reduce cathodically the compound at adjoining areas of the surface. This action is observed by a rapidly moving front of nonpassive iron increasing in area as more and more of the surface is activated. Bonhoeffer (2, 27) and his co-workers (18, 19) have studied in detail the mechanism of propagation of active-passive fronts as a model for nerve impulse propagation, following the earlier studies of passivity in this relation by Heathcote (28) and by Lillie (29).

Admission of halogen ions quickly breaks down passivity, possibly because these ions compete with the passivating compound for sites on the iron surface. Chloride ions adsorbed on iron have very short life (small activation energy for the corrosion reaction), contact with the surface being followed by rapid hydration and solution of metal ions. Such areas become anodes with subsequent progressive breakdown of passivity by electrolytic action, as noted above. It is also possible that chloride ions hasten reduction of the surface iron compound by reaction to form chlorine, or by some other mechanism.

The present conclusion that ferric acid or a related compound is responsible for passivity agrees with the deductions of Bonhoeffer, who suggested that the "oxide film" on iron passivated in nitric acid must have a higher oxygen dissociation pressure than any known normal oxide (2, 30). Ferric acid certainly fits into this category. It also agrees with the previous proposal of Bennett and Burnham (20) and of Bancroft and Porter (21) that a higher oxide FeO_3 appears to be necessary to explain their

passivation experiments and potential measurements. The present work shows indeed that an unstable, higher oxide exists. This work does not support the proposal of Vetter (31) that a common oxide of iron unsatisfied in composition with respect to its environment covers the surface, since such an oxide would not account for hexavalent iron or a structure analogous to the chromates.

Some investigators have concluded that the passive film on iron is a physical barrier layer consisting of Fe_2O_3 (32, 33). Support for this assumption was obtained in part by isolating an oxide film of the composition Fe_2O_3 using the iodine reaction or anodic dissolution techniques. However, an isolated film of Fe_2O_3, according to the present discussion, is merely an end product of the metastable hexavalent compound, and probably plays a small part, if any, in the passivation phenomenon. Ferric acid, for example, may decompose as follows:

$$2H_2FeO_4 \rightarrow Fe_2O_3 + 2H_2O + 3/2\ O_2$$

or

$$2Fe + 2H_2FeO_4 \rightarrow 2Fe_2O_3 + 2H_2O$$

On this basis, the maximum amount of ferrate found per apparent square centimeter of passive surface (2×10^{-8} mole/cm^2, Table IV) decomposes to a residual film of Fe_2O_3 ($d = 5.12$) 125 Å thick. The corresponding thickness, based on a reasonable roughness factor of 2 or 3, is 40–60 Å. These values agree approximately with optically determined values of 25–100 Å for the primary film reported by Tronstad and Borgmann (34), and with thicknesses for the decomposed primary film of 78 Å by microbalance weighings of Gulbransen (35), and with 80 Å by dissolution of oxide in acid as reported by Schwarz (36). The values are somewhat higher than 23 Å calculated by Vetter (37) from the amount of electricity required to reduce the passive film.

An explanation is still required for the function of urea and hydrogen peroxide in the passivation phenomena. In accord with the function of HNO_2 as depolarizer, enough iron must first react with nitric acid to produce a high concentration of nitrous acid near the metal sufficient for effective cathodic depolarization and corresponding achievement of the critical anodic current density for passivity. Consequently, if nitrous acid is added beforehand, as when potassium nitrite is added to nitric acid, iron becomes passive with much less than the normal amount of iron reacting. Urea destroys nitrous acid, but the reaction is not sufficiently rapid, as Vetter showed (11), to prevent build-up of nitrous acid at the metal surface by the iron-nitric acid reaction. Hence, approximately the normal amount of iron reacts with nitric acid plus urea to produce passivity, as the foregoing experiments show. After passivation, urea apparently succeeds in reducing the prevailing HNO_2 concentration at the surface and reduces the corresponding local action currents, thereby preventing repair of the adsorbed film, and causing loss of passivity, but only momentarily, because when larger anode areas form, nitric acid is more rapidly reduced at adjacent cathodes, HNO_2 again forms in greater concentration, and local action currents increase, followed by recovery of passivity. This situation accounts for periodic active-passive phenomena when iron is immersed in HNO_3-urea mixtures.

Hydrogen peroxide apparently reduces the concentration of nitrous acid by oxidizing it to nitric acid (38). It may also act to reduce ferric acid in the same manner it reduces chromates. Hence, periodic breakdown of passivity occurs, and more iron reacts during the 2-min immersion in concentrated HNO_3 containing H_2O_2.

As mentioned before, the metastable compound after adsorption on passive iron is not as easily reduced as properties of ferrates otherwise suggest, in the same sense that chemisorbed oxygen on tungsten is not easily reduced by hydrogen at elevated temperatures (39). Through chemisorption, both the metal and the adsorbate are passive to their environment, until such time as localized breakdown occurs in some portion of the passive film.

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Effect of Fluorides and Other Addition Agents on the Cathodic Potential of Titanium in Hydrofluoric Acid[1]

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ABSTRACT

The absolute hydrogen overvoltage values of titanium in hydrofluoric acid increase, or the cathodic potentials, η_{II}, decrease (become more negative) with addition of alkali fluorides to the acid. The η_{II} decreases with increasing concentration of the salt in the sequence $NH_4F \rightarrow KF \rightarrow NaF$, which is also the sequence of decreasing cationic radius. For example, at 50 ma/cm² η_{II} decreases from −0.8 v in pure 0.1*N* hydrofluoric acid to −1.68 v in the same acid if it is 1M with respect to sodium fluoride. If the titanium cathode dissolves in the acid, the η_{II}-current density relationship is linear; if the dissolution ceases (at higher concentrations of the added fluoride), Tafel's relationship is fulfilled. In between there is a mixed straight line and quasi logarithmic relationship, the latter occurring at higher current densities. Organic colloid solutions of agar-agar or arabic gum appreciably decrease η_{II}; methylene blue solutions increase it slightly.

Introduction

In connection with the general problem of titanium deposition from aqueous solution, consideration was given to the means of making the cathodic potential of the hydrogen-developing electrode as negative as possible. In other words, what conditions would increase the absolute value[2] of hydrogen overvoltage, which actually is a cathodic potential, thus favoring metal deposition?

First, the cathodic behavior of titanium was studied in pure bases and in hydrofluoric, hydrochloric, hydrobromic, sulfuric, and acetic acids (1). There was a straight line potential-current density relationship (equation I) in cases when the titanium cathode dissolved with an appreciable rate in the acid, evolving hydrogen in addition to that developed by the current. However, Tafel's logarithmic relationship (equation II) appeared if the titanium cathode did not dissolve in the acid, or if the dissolution rate was appreciably decreased (1, 2).

In order to study the lowering of the titanium cathode potential by use of different electrolytes, with the addition of different agents, and to compare the results, it was necessary to make the measurements with the same reference electrode. The 1*N* calomel electrode was chosen for this purpose, but the resulting potential measurements were reduced to the potential as compared to the standard hydrogen electrode. The cathodic potentials measured in this way are designated by η_{II}. The subscript II means that the potentials were measured in all cases against the same reference electrode, while hydrogen overpotential measurements (designation η) were usually made against a reversible hydrogen reference electrode immersed in the same solution (3) as that used for the electrolyte around the cathode. So the values η_{II} and η of an electrode in the same solution differ only by the effect of hydrogen ion concentration on the potential of the hydrogen reference electrode.

The cathodic potential (as well as the hydrogen overvoltage) on a metal in a pure electrolyte usually changes upon the addition of an organic compound to the electrolyte. Salt additions (4) may cause a decrease of the *a* constant of Tafel's equation (e.g., on mercury cathodes), although the *b* constants may remain unaffected (5, 6). The cathodic potential on copper and platinum in hydrofluoric acid is strongly decreased when ammonium fluoride is added to the acid (2). Organic compounds with oxidizing properties usually decrease the absolute value of hydrogen overvoltage (7).

The strong influence of soluble fluorides on the hydrogen overvoltage on platinum and copper (2) suggested the study of the cathodic potential of titanium in presence of water soluble fluorides.

Some experiments were also made with the addition of organic colloids.

Experimental Procedure and Materials Used

Of the two methods (8, 9) most commonly used for cathodic potential determinations, the "direct" method was chosen. This method is simpler, and,

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[2] For "absolute value" algebraic signs (of the potentials) are disregarded; "increase" means moving in a positive direction (more cathodic); "decrease" means moving in a negative direction (more anodic).

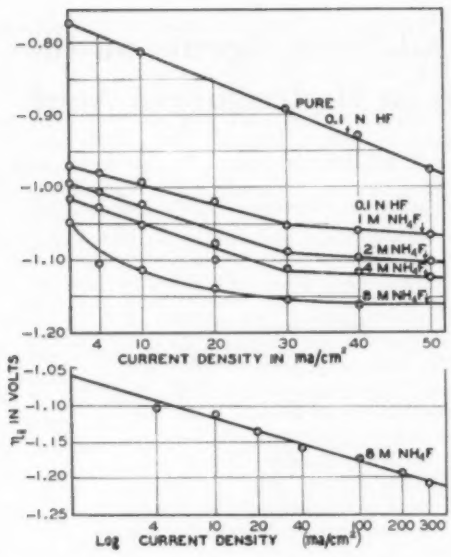

FIG. 1. Cathodic potential, η_{II}, of pure titanium in 0.1N HF with NH_4F added vs. current density and vs. log current density. Each experimental point is the average of two runs. Hydrogen scale.

according to authoritative views (8, 10), is as accurate and reliable as the "indirect" method, if applied correctly.

The electrolytic cell, made of a polyethylene beaker, contained the titanium cathode, a 2 x 2 cm platinum anode, and a stirrer making 375 rpm (11). The electrodes were mounted on a frame at a definite distance apart. The emf of the cell:

Ti // electrolyte / 3.5N KCl salt bridge / 1N KCl, Hg_2Cl_2 // Hg

was measured with a potentiometer equipped with a sensitive external galvanometer, while a current of a certain strength passed through the platinum anode and titanium cathode. The latter was cut from an iodide titanium crystal bar and had an exposed surface area of 1.8 x 0.85 cm². The glass handle of the electrode, as well as parts of the metal not to be exposed, were covered with a layer of Pyseal Wax to protect these parts from attack by hydrofluoric acid. The exposed surface was polished before each experiment through No. 00 emery paper, then etched by immersing the electrode in 1N hydrofluoric acid for about 1 min, followed by quick rinsing in distilled water. The end of the Luggin capillary was pressed horizontally and laterally against the titanium surface, thus preventing shielding of the metal by the tip itself.

No corrections, except reduction to the potential as determined against the standard hydrogen electrode, were introduced in the potential values measured. Consequently, values obtained with titanium in 0.1N hydrofluoric acid in the presence of various additions in different amounts represented cathodic potentials η_{II} of hydrogen evolution at a certain current density (1). As fairly strong currents were applied, the influence of atmospheric oxygen on the potential was so small (1, 12) that it was disregarded, and the air was not removed from the cell.

All chemicals were of reagent grade. The 99.99% iodide titanium (13) was supplied by the Foote Mineral Company.

RESULTS

Effect of ammonium fluoride.—Solutions for the electrolysis were prepared so that the concentration of hydrofluoric acid was kept constant at 0.1N, and the concentration of the ammonium fluoride was varied to give 1, 2, 4, and 8M solutions. The cathodic potentials measured are plotted against current density in Fig. 1. Ammonium fluoride additions decrease the cathodic potential of titanium, reaching a value of about −1.21 v (300 ma/cm²) in 8M ammonium fluoride solutions. The straight line relationship

$$\eta_{II} = a' + b'i \qquad (I)$$

holds up to 4M solutions, although a break occurs at about 30 ma/cm². In this equation a' is the potential of titanium at a current density $i = 0$, and b' is the slope constant. Equation (I) changes to the logarithmic or Tafel's relationship (14):

$$\eta_{II} = a + b \log i \qquad (II)$$

as the concentration of ammonium fluoride approaches and surpasses 4M (see lower curve of Fig. 1). The constant a in equation (II) is the potential of the titanium cathode at a current density of i = 1 ma/cm², and b is the slope constant of the Tafel lines.

It was observed that in 8M electrolytes the dissolution of titanium ceased almost completely. This indicates that the straight line relationship is maintained if the titanium dissolves in the acid, while the Tafel relationship holds if the titanium ceases to dissolve because of ammonium fluoride additions (1, 2). At low concentrations of this salt, up to 2M, a dark grayish scale was noticeable on the titanium electrode, and the solution became milky in appearance because of high dispersion of the evolved hydrogen; no scale could be detected at higher concentrations of ammonium fluoride.

Effect of sodium and potassium fluoride.—Sodium fluoride concentrations used were 0.02, 0.1, 0.2, 0.3, 0.5, and 1M, while the strength of hydrofluoric acid was kept at 0.1N. Sodium fluoride concentration was limited to 1M because of the low solubility of this salt in the acid. A summary of the results is given in Fig. 2, which shows that the addition of sodium fluoride has a very marked effect on the

cathodic potential. The straight line relationship [equation (I)] holds only at low concentrations of the fluoride; the linear portion of the curves becomes shorter and shorter with increasing concentration of the fluoride, while the remaining parts of the curve, especially the curves obtained with 0.3 to 1M solutions, obey Tafel's relationship [equation (II)]. The change from the straight line to the logarithmic relationship is accompanied by almost complete cessation of the dissolution of the titanium cathode in the acid. A dark grayish to slightly purplish scale appeared on the cathode at concentrations higher than 0.2M of sodium fluoride. Spectral analysis of the scale showed titanium with practically no sodium lines.

Curves obtained in 0.1, 0.5, 1, 2, and 8M solutions of potassium fluoride in 0.1*N* hydrofluoric acid were very similar to those shown in Fig. 2. The cathodic potential decreased strongly with the salt concentration, and the change from the mixed straight line-logarithmic relationship to the pure logarithmic one occurred between 1 and 2M concentration of potassium fluoride. Dissolution of the cathode in the latter solution ceased almost completely within 20 min after immersion of the electrode in the acidic solution. Scale formation was observed, but it decreased substantially in stronger fluoride concentrations.

Effect of complex fluorides.—A complex sodium titanium fluoride solution was prepared by adding cautiously a sodium fluoride solution to a titanium (III) fluoride solution, until the formation of a violet precipitate, probably of the composition Na_2TiF_5 (15), just started. Then the pink solution was diluted with hydrofluoric acid so that it became 0.1*N* and approximately 0.1M with respect to the Na_2TiF_5. A curve very similar to that obtained in 0.1M sodium fluoride (Fig. 2) could be drawn to represent the results from this solution. Hence, the presence of complex ions (pink color) did not change the curve from that obtained previously in sodium fluoride.

Effect of some colloids and organic substances.—The absolute value of the hydrogen overvoltage on metals is usually increased by the presence of organic colloids. This was also observed when a titanium cathode was used. The 0.1*N* hydrofluoric acid solution containing 0.1 wt % agar-agar (U.S.P. grade) was fairly viscous, but did not influence very much the cathodic potential of titanium. The current density-potential relationship could be described by equation (I) and the η_{II} values could be calculated in volts by equation (III)

$$\eta_{II} = -(0.83 + 0.0033i) \qquad \text{(III)}$$

up to $i = 30$ ma/cm², beyond which the potential

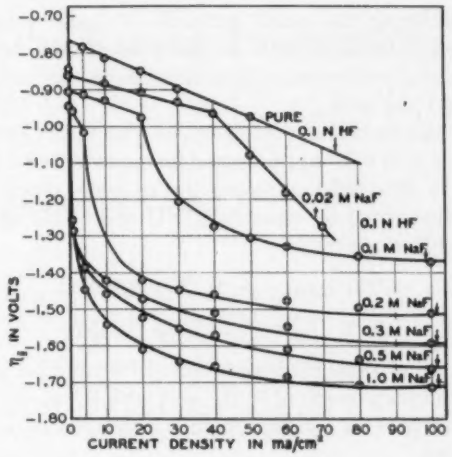

FIG. 2. Cathodic potential, η_{II}, of titanium in 0.1*N* HF with NaF added vs. current density. Each experimental point is the average of two runs. Hydrogen scale.

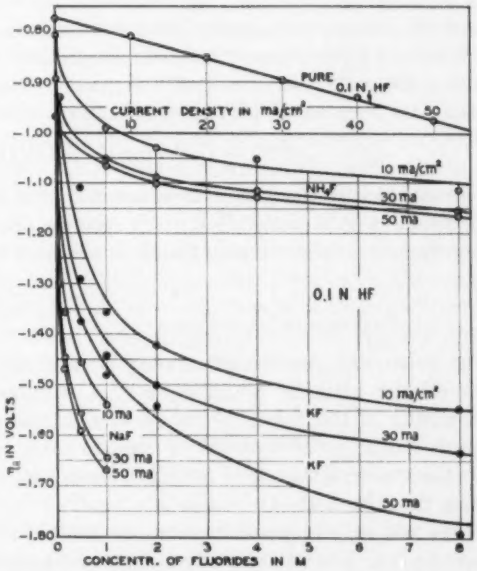

FIG. 3. Cathodic potential of Ti, η_{II}, in 0.1*N* HF vs. concentration of fluorides at constant current densities. Top inset: η_{II} vs. current density in pure 0.1*N* HF for comparison. Hydrogen scale.

readings fluctuated too much to obtain reliable readings.

A greater effect was observed with a 0.2% arabic gum solution (technical grade); the potential values conformed with equation (IV) up to $i = 50$ ma/cm²:

$$\eta_{II} = -(0.83 + 0.0077i) \qquad \text{(IV)}$$

The cathodic potentials obtained with titanium in pure 0.1*N* hydrofluoric acid (see Fig. 1 or 2) were more noble and corresponded to equation (V):

$$\eta_{II} = -(0.77 + 0.004i) \qquad \text{(V)}$$

Considering the small amounts of these colloids added to the acid, they are nearly as effective as the solutions containing sodium fluoride on the basis of weight per cent.

Methylene blue additions to the 0.1*N* hydrofluoric acid even in such small amounts as 0.005 and 0.02% by weight increased the cathodic potential, as represented by equations (VI) and (VII) up to $i = 100$ ma/cm²:

$$0.005\%\ \eta_{II} = -(0.72 + 0.0048i) \qquad \text{(VI)}$$

$$0.02\%\ \eta_{II} = -(0.58 + 0.0056i) \qquad \text{(VII)}$$

In all of these cases equation (I) is valid because the titanium dissolved in the acid with the evolution of hydrogen in addition to that developed by electrolysis.

Finally, a complex titanium citrate solution was used as an electrolyte in which the metal did not dissolve at all. In such a solution the Tafel relationship was obtained as expected. The clear solution contained 20 g titanium chloride, 260 g sodium citrate per liter, and some ammonium hydroxide so that the solution showed a pH = 8.7. The potential values agreed with equation (VIII) up to $i = 100$ ma/cm²:

$$\eta_{II} = -(0.93 + 0.045 \log i) \qquad \text{(VIII)}$$

As compared with the potential values in pure 0.1*N* hydrofluoric acid [equation (V)], the results are much more negative in the complex titanium citrate solution.

Discussion and Conclusion

Fig. 3 demonstrates the influence of fluoride additions on the cathodic potential, η_{II}, of titanium. Comparison of the potential values in solutions of varying molar concentrations of the fluorides reveals the strong influence of sodium fluoride, representing the salt effect (4).

There are several possible ways to explain the effect of alkali fluorides, but none of them is satisfactory. The negative potential of the titanium electrode [a' constant of equation (I)] may be caused by the very low concentration of Ti^{3+} as a result of complex ion formation with the fluorides added (2). However, if this is so, at equal concentrations of the three fluorides, nearly the same potential-current density curves should be expected; however, this is not the case as can be seen in Fig. 3. That there is a specific effect of the fluorides on the overvoltage, independent of the Ti^{3+} or Ti^{4+} concentration, is indicated by the fact that the absolute overvoltage values on copper and platinum also increased in the presence of ammonium fluoride (2). Another explanation of this salt effect is given by deBéthune (4).

Adsorption phenomena as well as formation of some oxide and salt layers on the titanium cathode may be responsible for the increased overvoltage. This is possibly correct in the case of the addition of organic colloids to the hydrofluoric acid, as only weak currents of 50 ma/cm² maximum were obtained through the cathode without fluctuation. However, tests showed that such colloids, dissolved in 0.1*N* hydrofluoric acid, added to pure acid solutions through which a current is already flowing, decreased the current only a small amount.

If fluorides are added to the acid, the conductivity of the electrolyte increases and, under comparable conditions, currents up to 300 ma/cm² could be passed through the cathode. This certainly would not be possible if oxide or salt layers were present in any appreciable amount on the titanium surface. Visual examination of the electrodes showed that layers are not noticeable at higher concentrations of potassium and ammonium fluoride. Finally, it follows from Fig. 3 that the cathodic potential values decrease with decreasing cationic radius, $NH_4^+ \rightarrow K^+ \rightarrow Na^+$, of the fluoride added, the radius being obtained from x-ray data. The sizes of the hydrated ions were discussed by Bockris (16).

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Influence of Specimen Area on the Pitting Probability of Aluminum[1]

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ABSTRACT

The pitting probability of 2S aluminum was determined in Kingston tap water as a function of area, for areas ranging in size from 0.06 cm² to 243 cm². The pitting probability was found to vary uniformly with area, from 0.001 to 1 as the area increased from 0.06 cm² to 60 cm²; extrapolation indicated that the pitting probability becomes zero at an exposed area of about 0.055 cm². This work supports the contention that pitting sites in aluminum are not specific macrodefects in the metal surface, but rather arise in a random fashion through the interaction of myriads of anodic and cathodic elements on the metal surface.

Introduction

Previous publications (1, 2) have reported the development of a theory of the pitting corrosion of aluminum. In this work it has been shown that when a sheet of aluminum is immersed in a natural water that is aggressive, pitting-wise, the initial attack takes the form of general corrosion so that the surface is covered with myriads of local cells. As reaction proceeds, aluminum goes into solution at the local anodes, while alkali forms at the local cathodes through reduction of oxygen and hydrogen ions. As the anodic and cathodic reaction products intermingle, alumina is precipitated from solution, stifling the reaction and passivating the surface, through the formation of a protective film. If the precipitation of alumina does not completely stifle the local cells, then reaction can continue with a consequent continuing modification of the environment about the sites of the reactions. These environmental changes further stimulate local action so that the attack is autocatalytic in nature and those local cells that have survived consequently develop into pits. An autocatalytic mechanism of pitting corrosion very similar to the one here presented has been developed by Edeleanu and Evans (3) from electrochemical measurements carried out on two-compartment cells. If this picture is correct, local environmental differences must be established and maintained if a pit is to initiate and propagate. These environmental differences will be maintained by the local action currents and dissipated by convection and diffusion so that, for any given set of experimental conditions, it is to be expected that a minimum local action current will be required to initiate and maintain pitting. Support for this comes from the fact that a moderate movement of water over the surface reduces the incidence of pitting and, at only 8 fpm, pitting is completely prevented in an otherwise aggressive medium (4).

As the corrosion of aluminum has been shown to be under cathodic control a reduction of the total area exposed will reduce the local current since it will reduce the available cathode area.

Thus, on this view of pitting corrosion the pitting probability should decrease as the sample area exposed is reduced and should become zero at some small value of the exposed area.

The influence of area on corrosion probability has been studied by Mears and Brown (5). Their work, however, did not cover a range of areas sufficient to test the authors' hypothesis that the pitting probability becomes zero at some small finite value of the area.

Experimental

Since this work was carried out to determine whether there is a minimum area required to sustain pitting, attention was confined to pits actively propagating in tap water at the end of a week.

Description of Material

2S aluminum of the composition shown in Table I was employed throughout this investigation. The metal, obtained in the form of full hard sheets 0.064 in. thick, was sheared into 8 in. x 6 in. panels and annealed for ½ hr at 400°C preparatory to use.

The corrosive medium employed throughout was Kingston tap water, the composition of which is given in Table II.

Procedure

The panels were etched in phosphoric acid at 70°C for 2 min, washed in running tap water for 20 min, and air-dried for 15 hr. The surface of an 18.1 x

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TABLE I. *% Composition of metal used*

Cu	Fe	Si	Ti	Al (by difference)
0.02	0.55	0.13	0.015	99.29

TABLE II. *Composition of Kingston tap water*

	ppm
pH	8.0
Residue on evaporation	161
Total hardness	127
Bicarbonates as HCO_3	113
Sulfates as SO_4	22
Chlorides as Cl_2	16
Calcium	37
Magnesium	8
Silica	4
Iron	0.05
Copper	0.015
Electrical conductivity	270 recip. megohms at 20°C

TABLE III. *Square sizes studied*

Size of square	Square area	Squares per panel
cm	*cm²*	
0.25 x 0.25	0.06	3858
0.50 x 0.50	0.25	912
0.75 x 0.75	0.5	432
1.0 x 1.0	1.0	252
1.5 x 1.5	2.2	108
4.5 x 3.4	15	16
4.5 x 6.75	30	8
9 x 6.75	61	4
9 x 13.5	122	2
18 x 13.5	243	1

TABLE IV. *Pitting probabilities and total number of pits measured*

Total No. of squares	Size of square	Area of square	Pitting probability	Total No. of pits	Probability of obtaining one pit‡
	cm	*cm²*			
14,432	0.25 x 0.25	0.06	0.001	46	0
3858	0.50 x 0.50	0.25	0.10	604	0.15
1728	0.75 x 0.75	0.56	0.25	724	0.38
1008	1.0 x 1.0	1.0	0.47	644	0.55
432	1.5 x 1.5	2.25	0.50	293	0.42
64	4.5 x 3.4	15.2	0.88	339	0.14
32	4.5 x 6.75	30.4	0.91	219	0.03
16	9 x 6.75	61	1	376	0
8	9 x 13.5	121	1	238	0
4	18 x 13.5	243	1	321	0

13.5 cm area of the panel was then divided into the requisite number of squares with wax solution (Xylol saturated with paraffin at 30°C) preparatory to exposing the samples. The various square sizes employed are given in Table III. Wax lines were applied to the panels with 1, 2, 4, 8, and 16 squares with an ordinary ruling pen. The remaining panels were prepared by stamping a wax grid onto the surface with a rubber stamp (6). The wax was permitted to dry for 15 hr and then drops of tap water were placed in each of the squares formed by the grid. The panels were placed for seven days in a closed space over water as previously described (7), then removed, washed, and dried. The number of pits in each square was counted and the pitting probabilities computed. Four panels of each square size were exposed simultaneously.

Results and Discussion

The probability of obtaining one or more pits per square, and the probability of obtaining only one pit per square were computed from the experimental data and are recorded in Table IV. In addition, the total number of pits developed at each level of subdivision is also presented.

These data are also presented graphically as a function of the logarithm of the surface area exposed at each square size in Fig. 1.

Examination of this figure shows that as the area exposed decreases from 243 cm² the pitting probability remains constant at a value of 1 until the area has decreased to a value of about 60 cm². Thereupon the probability decreases with decreasing area until it reaches a value of 0.001 at an area of 0.06 cm². If the curve of the total number of pits developed is extrapolated to zero, it will cut the axis at an area of about 0.055 cm²; thus, at and below this value the pitting probability is zero. Hence it may be concluded that an exposed area of at least 0.055 cm² is required for the initiation and propagation of a pit under the conditions of the experiment.

These results are considered good evidence in favor of the view that pitting is due to a mechanism of the type presented in the introduction to this

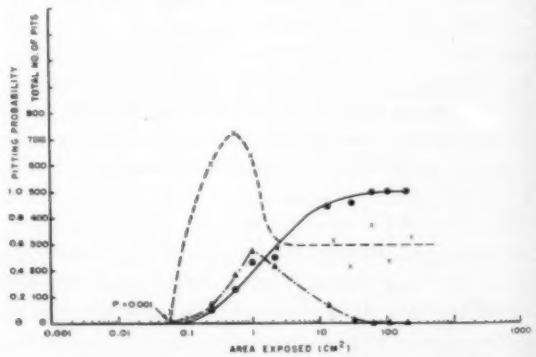

Fig. 1. Pitting probabilities and total number of pits developed as a function of area. ▲——▲, Probability of one pit vs. area; ●——●, pitting probability vs. area; ×——×, total number pits vs. area.

paper in which pitting is considered to be due not to specific macrodefects in the surface of the sheet, but rather to the prevention of complete passivation of the metal surface because of environmental differences set up through the agency of local action currents flowing over the surface of the metal.

It is interesting to examine the dependence of the total number of pits developed on four panels on the degree of subdivision. This remains essentially constant with decreasing area until an area of about 5 cm^2 is reached, whereupon the number of pits starts to increase, goes through a maximum, and falls rapidly to zero.

These results can be explained as follows. The total number of pits on a fixed area remains constant as long as the linear dimensions of the individual squares are greater than the distances over which the pits interact with each other. When the dimensions of the waxed squares become less than these interaction distances, then the total number of pits increases because interaction and suppression of pits between areas that originally pitted and areas that did not pit is now prevented by the wax lines and hence originally unpitted areas can now pit. When these dimensions are decreased still further so that the size of the waxed-off areas approaches the minimum required to sustain pitting the total number of pits falls.

The maximum probability that a square will contain one pit occurs at a size of 1 cm^2. Since the pits were observed to be distributed randomly within the waxed-off squares, the maximum distance of influence of a pit is about $\sqrt{2}$ cm, in other words, it will draw current from a cathode area of about 1 cm in radius under the conditions studied.

It should be pointed out that the positions of the maxima and the shape of the curves will depend on the medium employed and especially on its conductivity, since changes in conductivity alter the extent of the cathode area from which the pit can draw current.

Furthermore, more aggressive solutions or those of greater conductivity than the one herein employed permit greater local action currents to flow during the initial stages of attack and hence environmental differences are more easily established so that a smaller exposed area is necessary to sustain pitting than that found in this work. Similarly, smaller local action currents would flow in solutions less aggressive or of lower conductivity than the tap water here employed and under these conditions a larger area would be needed to sustain pitting.

The experimental results reported here substantiate the views developed in the introduction to this paper and are considered good evidence that pit sites are not due to specific local macrodefects in the surface of the metal, but rather arise in a random fashion through the interaction of myriads of anodic and cathodic elements on the metal surface between which local action currents flow on initial immersion of the sample in the corrosive environment. The net result of this interaction would be the production of an insoluble corrosion product which can be precipitated in one of the three following ways leading to the three types of behavior indicated:

(*A*) The corrosion product may be precipitated in contact with the metal surface completely passivating it and stifling reaction.

(*B*) The corrosion product may be precipitated in contact with the metal surface but incompletely passivating it, causing a localization of the attack and thus leading to pitting.

(*C*) The corrosion product may be precipitated out of contact with the metal surface leading to general corrosion.

If (*B*) occurs, the case in which we are here interested, it can be seen that pit sites will be distributed in a random fashion.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Electron Microscope Studies on Copper Deposits from Sulfate and Cyanide Baths[1]

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ABSTRACT

Copper deposits from sulfate and cyanide baths, at low current densities, show lack of uniformity on various cathodes. The crystal structure of the base metal has a profound influence on the nonuniformity, which is characteristic for a given single crystal cathode, but differs markedly for the two different electrolytes. Planes parallel to (010) and (111) planes of the base crystal develop in a copper sulfate bath while, in a cyanide bath, planes develop parallel to the (130) plane of the base crystal.

INTRODUCTION

It has generally been considered that deposition of copper on a copper cathode tends to perpetuate the structure of the base metal. The relation between crystal growth and number of nuclei has been studied by Glazunov (1), while Takeyama has reported that, under favorable conditions, the copper deposited in the early stages of deposition consisted of a nearly perfect single crystal (2).

The present study was made to determine the orientation of the deposit relative to that of the base metal, by means of the electron microscope. This approach presented two problems. One was the reproducibility of replicas, the other was to locate the identical spot on the cathode under the electron microscope before and after electrolysis. Satisfactory experimental solutions to these problems have been discussed elsewhere (3) and need not be detailed here.

EXPERIMENTAL

The copper sulfate bath contained 150 g/l copper sulfate pentahydrate and 40 g/l sulfuric acid. The cyanide bath contained 22.5 g/l copper cyanide, 30.0 g/l sodium cyanide, and 10.0 g/l sodium carbonate. Electrolysis occurred, without agitation, at 30°C in all experiments. The anodes were 2 cm x 2 cm rolled copper plates, while the cathodes were copper plates, characteristics of which varied for different experiments. One side of each anode and cathode was coated with polyvinyl formal.

The negative replica method was used for electron microscopy. A benzol solution of polymethyl methacrylate was poured on the surface of the electrode before electrolysis and allowed to dry. The resin film was then carefully removed from the electrode, placed in a vacuum evaporator, first coated with aluminum and then shadowed with chromium in the usual manner. After deposition, the electrode was successively rinsed with distilled water and ethanol, dried, and again treated with polymethyl methacrylate as outlined above. The technique outlined previously (3) was used to locate the identical spot on the electrode under the electron microscope before and after electrolysis.

RESULTS

Deposition from Copper Sulfate Electrolyte

On electropolished rolled copper.—Copper was deposited on the electropolished surface of a rolled copper plate, 2 cm x 2 cm in area and 0.5 mm thick, at current densities between 20 ma/cm² and 1.6 ma/cm². The deposit was almost uniform over the cathode, at higher, but not at lower, current densities. The lower the current density the more exaggerated was the nonuniformity. The electrolysis at higher current densities has been discussed earlier (4), and only the results for lower current densities are discussed here.

In Plate I (*a*) is shown the initial surface of a copper electrode that has been electropolished in 50% phosphoric acid solution, in preparation for electrolysis. The "pine needle" appearance was characteristic of all specimens prepared in this way.

Electrodeposition for 2 min at 1.6 ma/cm² gave the nonuniform deposit shown in Plate I (*b*), which, on further electrolysis for 22 min, gave the accentuated unevenness of Plate I (*c*). If it is assumed that the deposit is uniform over the surface, and that the current efficiency is 100%, the thickness of the deposit is about 1 μ.

The nonuniformity of the deposit is believed to be due to preferential discharge of copper ions at different rates at the most readily accessible points on differently oriented crystals of the base metal. Under an optical microscope, it appeared that uniform portions of the surface carried no deposit and

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that the uneven parts were due to "islands" of the deposit.

PLATE I(*a*). ×2600

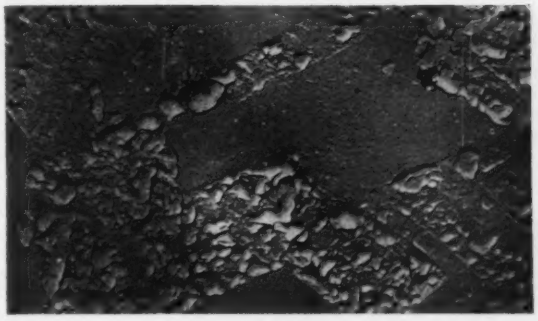

PLATE I(*b*). ×2600

PLATE I(*c*). ×2600

PLATE II. ×2600

On chemically etched rolled copper.—Copper was deposited at current densities between 20 ma/cm² and 1.6 ma/cm² on a rolled copper cathode etched with 10% ammonium persulfate to reveal the (100) planes (5). The nonuniformity of the deposits was again observed at the lower current densities, as shown in Plate II.

On annealed copper.—With the rolled cathodes used in the previous experiments it was not possible to discern each crystal of the base metal clearly. It seemed possible that the rolling process had strained the metal in the cathodes, and the strains might have affected the deposits. A study was made, therefore, of the nature of deposits on rolled cathodes which had been annealed at 800°C for 5 hr to induce

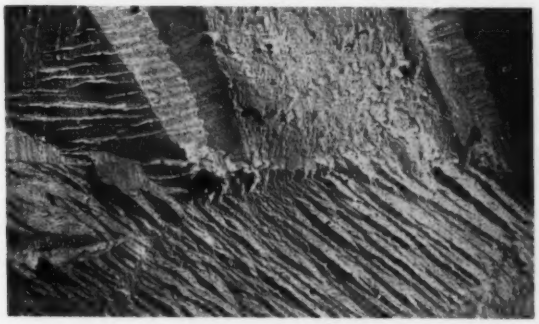

PLATE III(*a*). ×2600

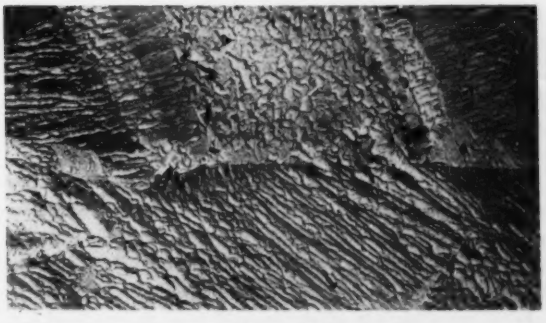

PLATE III(*b*). ×2600

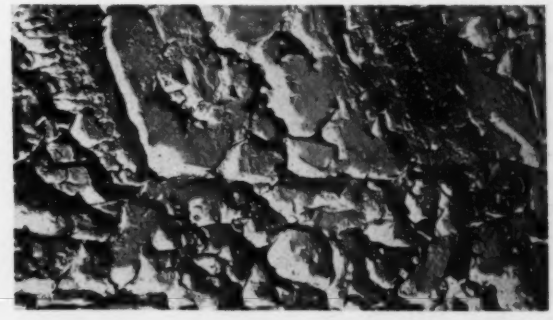

PLATE III(*c*). ×2600

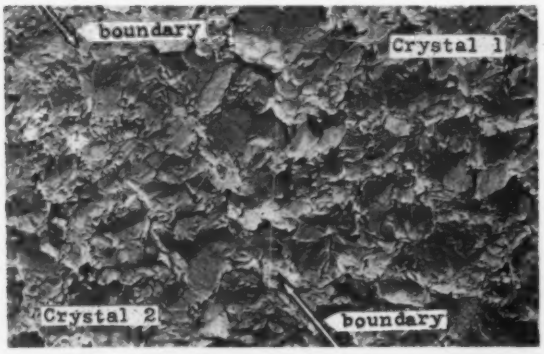

PLATE IV(*a*). ×3000

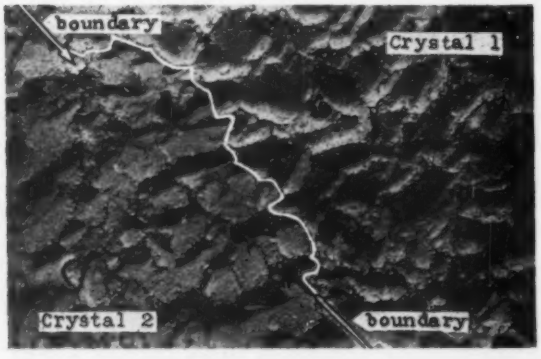

PLATE IV(*b*). ×3000

larger crystals and relieve working strains. The initial surface of these cathodes, after etching with 10% ammonium persulfate, is shown in Plate III (*a*). After electrolysis at 1 ma/cm² for 3 min, the surface depicted in Plate III (*b*) was obtained. Further electrolysis for 30 min gave the surface revealed in Plate III (*c*). The isolated patches of deposit, characteristic of Plate I, did not appear, and the surface of the deposit was of uniform appearance. It appears that strains present in the rolled cathodes were, indeed, responsible for the lack of uniformity in deposits on such cathodes, and that the nature of the deposit over a given crystal was determined by the underlying crystal.

On single crystal-copper.—To determine the relation between the orientation of the deposit and the crystal orientation of the base metal, copper was deposited on an electropolished cathode composed of two single crystals of known orientation. The cathode shows the pine needle design, with no crystal boundary evident, characteristic of the electropolished surface. After electrodeposition for 17 min at 1 ma/cm², the surface assumed the condition shown in Plate IV (*a*), where the crystal boundary is discernible. The boundary became accentuated after 53 min additional deposition, as shown in Plate IV (*b*); this is shown more clearly by the greater magnification of Plate V. The ability

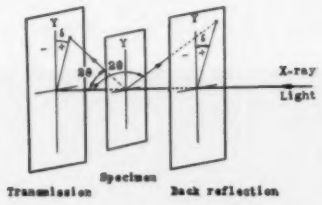

FIG. 1

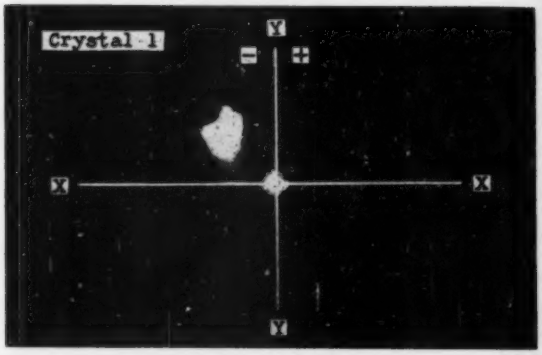

FIG. 2(*a*)

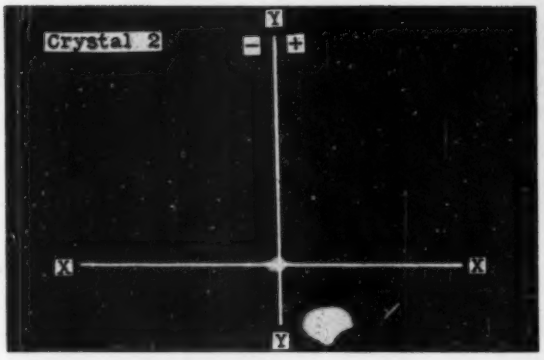

FIG. 2(*b*)

to distinguish the boundary after deposition shows that the deposits on the two crystals were different.

To determine the orientation of the mozaic blocks composing the two deposits, ordinary light reflected from the crystal facets of the electrodeposit was used as a means of establishing the position of the facets relative to a certain arbitrary set of axes (6). Then, with the crystal in the same position and using transmitted x-ray, the orientation of the original single crystal which was used as the base metal was determined. By comparison of the two sets of data it was learned which planes in the original base-metal crystal were approximately parallel to the facets of the electrodeposit. The x-ray study, however, does not yield information on the crystal orientation of the electrodeposit; such information can be obtained only by electron diffraction.

The two methods are illustrated schematically

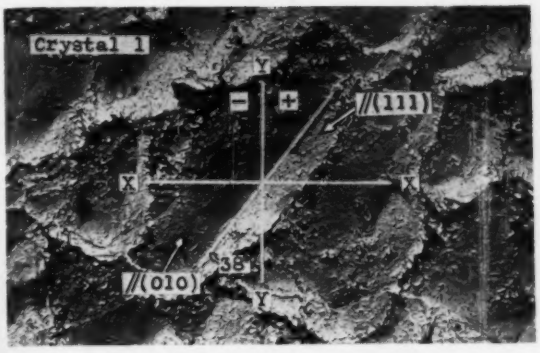

PLATE V(*a*). ×5900

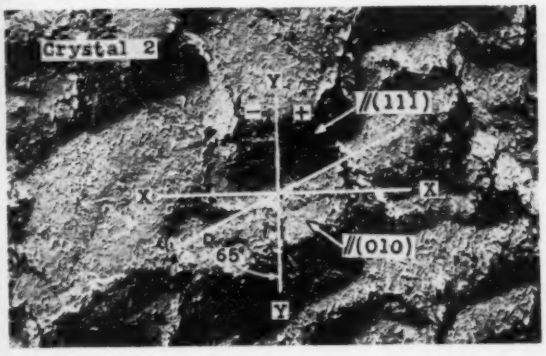

PLATE V(*b*). ×5900

TABLE I (*a*)

			Crystal 1		Crystal 2	
			δ	θ	δ	θ
Sulfate bath	Deposit on polished surface	Optical	−40° (P_1)	72°	145° (P_2)	73°
	Deposit on etched surface	Optical	−40° (E_1)	72°	142° (E_2)	73°
	Index of (010) of base crystal	X-ray	−40°	68°	145°	65°

TABLE I (*b*)

			Crystal 1		Crystal 2	
			δ	θ	δ	θ
Sulfate bath	Deposit on polished surface	Optical	113° (P_1')	59°	−14° (P_2')	59°
	Index of (111), (11$\bar{1}$) of base crystal	X-ray	114° (111)	56°	−9° (11$\bar{1}$)	58°

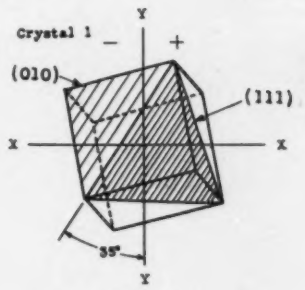

FIG. 3(*a*)

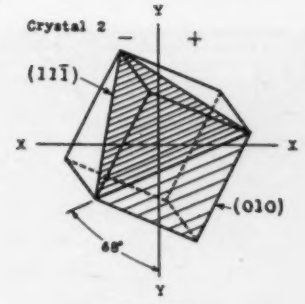

FIG. 3(*b*)

in Fig. 1. The specimen was not rotated for the optical examination, and the reflected light was received on a photographic plate rather than observed visually. Optical data were directly comparable with the transmission data; these are recorded in Table I (*a*) and (*b*). The patterns of the back reflection from the deposits on crystals 1 and 2 are shown in Fig. 2 (*a*) and (*b*), respectively. It will be noted that the reflection spread considerably, with the 0.5 mm aperture used, probably because of imperfect orientation of the facets of the deposit. In Fig. 3 (*a*) and (*b*) are shown the corresponding unit cells for crystals 1 and 2, as determined from x-ray patterns. In Table I, the δ and θ values for the base crystals, from the x-ray analysis, show only the index of the plane in the original crystal which most nearly corresponds to the plane of the reflecting facet of the deposit, as given by the reflection with ordinary light.

When the single crystal-cathode was etched with 10% ammonium persulfate, rather than electropolished, and electrodeposition continued for 2 hr at 1 ma/cm², the optical back reflection gave results comparable with those obtained on the electropolished crystals (Table I).

It might be noted that, although the results in Table I are for intermittent electrolysis, the same results were obtained by continuous electrolysis.

Deposition from Copper Cyanide Electrolyte

On electropolished and etched rolled copper.—Copper

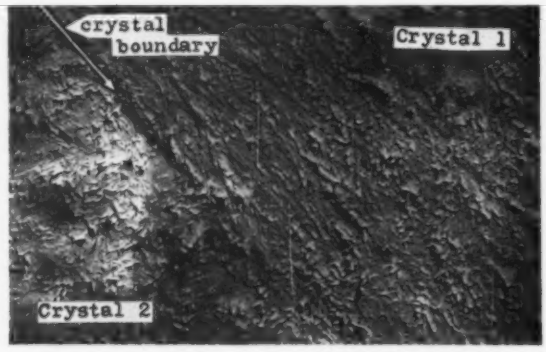

PLATE VI(*a*). ×4000

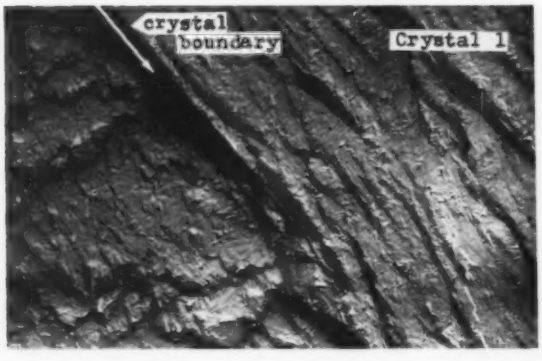

PLATE VI(*b*). ×4000

was deposited from a cyanide bath on rolled copper cathodes at current densities between 10 ma/cm² and 1.6 ma/cm². Regardless of whether the cathode had been electropolished or chemically etched, in the manner of the earlier experiments, no nonuniformity of the deposit was observed at any current density. All the deposits were very fine in crystal grain and smooth.

On single-crystal copper.—To determine whether the deposit from a cyanide electrolyte would show a characteristic plane on a single-crystal cathode, copper was deposited on the electropolished bi-crystal cathode described previously, at 0.5 ma/cm². The initial surface of the cathode again did not reveal the crystal boundary.

After electrolysis for 30 min, however, the boundary became evident [Plate VI (*a*)], and further electrolysis for more prolonged periods made it much more pronounced [Plate VI (*b*), electrolysis time of 150 min]. Plates VII (*a*) and (*b*), show the surface corresponding to Plate VI (*b*) under greater magnification. It is clear from the evidence presented that the deposit was influenced by the orientation of the base crystal. Data for the optical back reflection of the deposit and x-ray examinations of the base crystals respectively are given in Table II. As before, x-ray data show which plane in the base crystal has indices nearest to those of the facet of the deposit that gave the back reflection. Again, data for intermittent electrolysis were the same as those for continuous electrolysis.

TABLE II

			Crystal 1		Crystal 2	
			δ	θ	δ	θ
Cyanide bath	Deposit on polished surface	Optical	−105° (P_1)	78°	−165° (P_2)	78°
	Deposit on etched surface	Optical	−102° (E_1)	80°	−165° (E_2)	80°
	Index of (130) of base crystal	X-ray	−100°	80°	−170°	77°

When the single-crystal cathode was chemically etched, electrolysis in the cyanide bath for 2 hr at 0.5 ma/cm² yielded a deposit for which the back reflection values are those shown in Table II.

DISCUSSION

Deposition from copper sulfate electrolyte.—The data of Table I are summarized stereographically in Fig. 4. P_1 and P_2 represent the normals to the

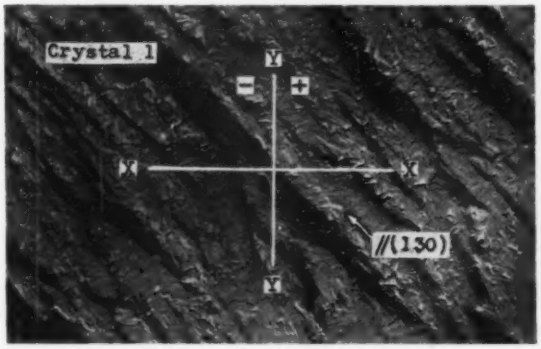

PLATE VII(*a*). ×3700

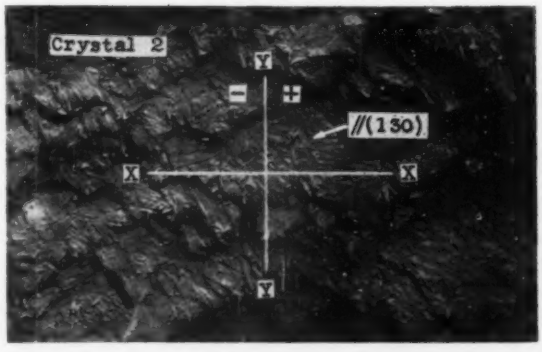

PLATE VII(*b*). ×3700

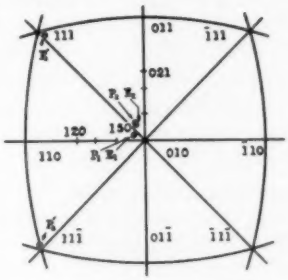

FIG. 4

optical reflecting facets for the deposit on the electropolished crystals 1 and 2, respectively. E_1 and E_2 represent the corresponding facets for the deposit on the etched crystals 1 and 2. While the four points conceivably represent the (171) plane, it is adequate to associate them with the simpler (010) index. The optical back reflecting facets of the deposit on crystal 1, with the normals P_1 and E_1, are heavily shadowed planes of Plate V (*a*), and these are parallel to the (010) plane of the base crystal. From Table I (*b*), the lightly shadowed planes of Plate V (*a*) are considered to be parallel to the (111) planes of the base crystal. The back reflection facets of the deposit on crystal 2, with the normals P_2 and E_2, are the lightly shadowed planes of Plate V(*b*), and these planes are parallel to the (010) planes of this base crystal. From Table I (*b*), heavily shadowed planes

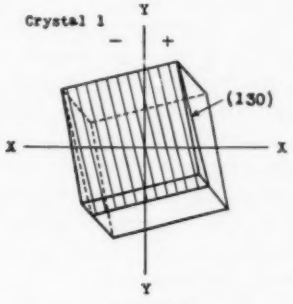

FIG. 5(*a*)

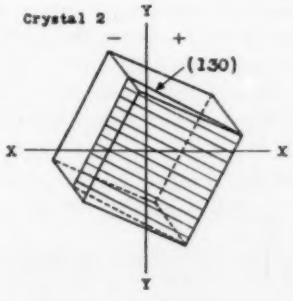

FIG. 5(*b*)

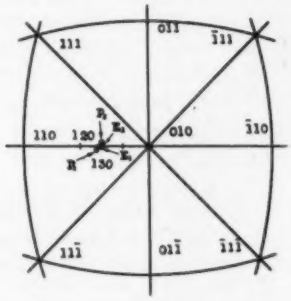

FIG. 6

are thought to be parallel to the $(11\bar{1})$ planes of the base crystal.

It is concluded that the deposition from a sulfate bath on a single crystal occurs with planes parallel to the (010) and (111) planes of the base crystal.

Deposition from copper cyanide electrolyte.—The data of Table II are summarized stereographically in Fig. 6. As before, P_1 and P_2 represent the normals to the optical back reflecting facets for the deposit on the electropolished crystals 1 and 2, respectively, and E_1 and E_2 the corresponding facets on the chemically etched crystals. The normals to these facets are near the normal to the (130) planes of the base crystal. Hence, the back reflecting facets are parallel to the (130) plane of the base crystal. Fig. 5 (*a*) and (*b*) shows a unit cell of the base crystals 1 and 2, corresponding to Plates VII (*a*) and (*b*). The lightly shadowed planes in Plates VII (*a*) and (*b*) are parallel to the (130) plane of the base crystal, shown by hatching in Fig. 5 (*a*) and (*b*).

It is concluded that the deposit from a cyanide bath on a single crystal shows planes parallel to the (130) plane of the base crystal.

ACKNOWLEDGMENTS

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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A Study of the Etching Rate of Single-Crystal Germanium[1]

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ABSTRACT

A study has been made of the rate at which single-crystal germanium is etched under various conditions. For simplicity, the principal etchants used were composed of only H_2O_2, HF, and water. Data are given for the rate as a function of temperature and composition of the etchant, and as a function of the orientation and impurity content of the crystal. An equation which assumes two reactions taking place in sequence on the surface fits the rate vs. temperature data within the limits of experimental error. In the range studied, the rate-controlling processes are sensitive to sample orientation. From etching data, a value was obtained for the thickness of the disturbed surface layer due to abrasive grinding. This was found to be in the range of 2–10 μ and to depend on sample orientation and abrasive particle size. Comparative data are given for two common etchants of a more complicated composition.

INTRODUCTION

For several years, the treatment of germanium by etching has played an important role in the production of germanium devices and in the preparation of samples for research purposes. In the last two years, such treatment has become an increasingly important tool for investigating the orientation and quality of germanium samples, different treatments revealing different properties of the material. But the treatments themselves have not been well understood. In the hope of progressing toward an understanding of these processes, a study has been made of the etching rate of germanium crystals under various conditions. For simplicity, most of the work has been confined to etchants containing only HF, H_2O_2, and water. In order to insure sample uniformity, all samples were cut from one large single crystal of As-doped, *n*-type germanium. Since the resistivity of the crystal varied slowly along its length, resistivities between 1 and 9 ohm-cm could be obtained by selecting samples from the proper region of the crystal. The samples were thin, usually of the order of 30 mils thickness, so that the ratio of face area to edge area was large. The error introduced by including the edge area as if it were of the same orientation as the face was less than 2%. The samples were held with polyethylene-coated tweezers and the area of contact was small enough to be neglected. Etching rates were obtained by measuring the loss of weight of a sample after a known etching time. Weights were measured to 0.2 mg and the weight differences were usually of the order of 20 mg. Considerable attention was given to the freshness and composition of the etchants and to the surface preparation of the samples. In order that the circulation of the etching solution should not influence the results, all experiments were performed under conditions of agitation sufficiently violent that substantial changes in agitation made no difference in the etching rate.

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GENERAL PRECAUTIONS

Since little was known about the effects of various parameters on the etching rate, much effort was devoted to insuring that only the parameter under investigation was influencing the results. This was done either by comparison of samples differing in only one respect, or by direct experiment to determine what parameters could be ignored safely.

Temperature.—The temperature was maintained constant by immersing the etching vessel in a constant temperature bath. The volume of etchant used, about 60 cc, was large compared to the volume of the samples. The temperature of the etchant was measured directly to ± 0.3°C by means of a polyethylene-coated thermometer.

Resistivity.—The samples used were kept short so that the variation in resistivity along the length was less than ± 5% from the mean except for the 1 ohm-cm sample. Insofar as possible, samples were compared which were cut from the same depth in the crystal. All samples were labeled to show from what part of the crystal they came. Thus, the notation 4(100)3-2 means that the sample was from the fourth resistivity region of the crystal, a (100) cut, and the third slab from the surface. This sample was then cut into smaller pieces, the -2 indicating the second such piece.

Etch composition.—Etches were made up fresh

each day in batches large enough that the composition was measured with an accuracy greater than the assay of the reagents used. Most work was done with the simplest etch (1 HF, 1 H_2O_2, 4H_2O), called the No. 2 etch (see appendix for etch compositions). The variation in the concentration of the reagent H_2O_2 used (5 parts in 30) was sufficient to introduce a rate error of about ±4%. However, in most experiments, the same reagent was used. Therefore, although the absolute values may have been affected, the accuracy of the comparisons was determined by other factors.

Faust (1) reported that the presence of polyethylene in contact with the HF-H_2O_2 etch increases the reaction rate. Both the reagent HF and H_2O_2 in the present study were stored, prior to use, in polyethylene bottles. To determine stability, a stock solution of No. 2 etchant was kept in a polyethylene bottle for an additional six weeks; the rate measured at the end of this period was the same as that measured at the start. This indicates that etching solutions may actually be made up in large quantities and used over a considerable period of time.

Weighing.—Etching rates were obtained by measuring the loss of weight of the sample during a measured time of etching. Weights were measured to ±0.2 mg. Weight differences were usually of the order of 20 mg.

Agitation.—In order to make certain that the rate of agitation used did not influence the results, a set of measurements was made of the weight loss of a sample etched under different conditions of agitation. This experiment was done at 40°C, a temperature at which the rate of etching was known to be high. The curve is shown in Fig. 1. One agitation is a movement to and fro of 1 in. in a 60-cc beaker containing 40 cc of solution, and it is seen that one or two agitations per second are enough to stabilize the etching rate. All subsequent measurements were made at a rate of 2–4 agitations per second, well above the critical region.

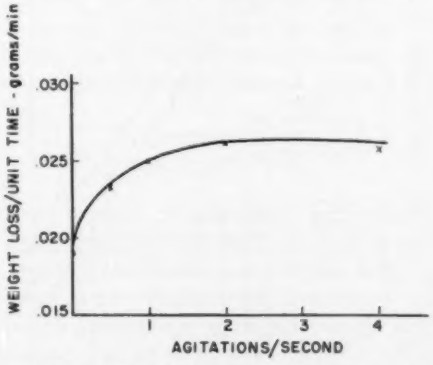

FIG. 1. Effect of agitation on the etching rate. (One agitation is a movement to and fro of 1 in.)

Surface preparation.—Most samples were fine-ground with American Optical Company No. 305 abrasive and all were pre-etched for 5–20 min in No. 2 etch at room temperature. As will be seen in the next section, this was apparently more than sufficient to remove the disordered surface layer.

RATE VS. TIME OF ETCHING

A number of thin samples was prepared by uniformly grinding their surfaces with No. 305 abrasive in water on a glass plate. They were weighed, etched for a short time in No. 2 etch at constant temperature, and weighed again. The average etching rate for this interval was then computed. The etching and weighing process was repeated until the rates became constant. Average rates were plotted at the mid points of their respective intervals and a rate-vs.-time curve obtained. A representative sample of the experimental results is shown in Fig. 2. The values shown are for three differently oriented samples cut from the same 9 ohm-cm crystal. A second set of data, obtained with 1–6 ohm-cm samples, resulted in similar curves, as did data for these samples ground with a coarser abrasive (No. 303½).

The following explanation can account for the shape of the experimental curves, the measured

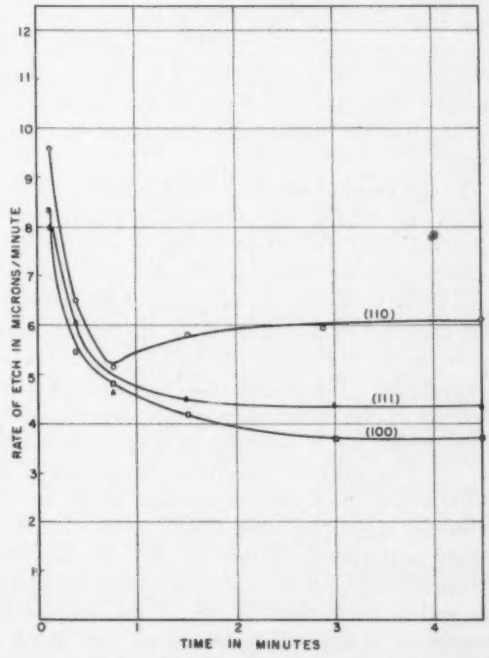

FIG. 2. Rate of etching as a function of time of etching and crystal orientation. Before etching was begun, the surface was finely ground with No. 305 abrasive.

TABLE I. *Thickness of disordered layer vs. crystal orientation*

Sample	Approximate thickness of disordered layer in microns, for surface indicated		
	(100)	(111)	(110)
Set 1. 9 ohm-cm No. 305 Abrasive.....	7	5	3
Set 2. 1-6 ohm-cm No. 305 Abrasive...	5	4	3
Set 2. 1-6 ohm-cm No. 303½ Abrasive.	10	10	5
Predicted relative values (see text)....	10	0–12	5

thickness of the disordered layer, and its dependence on particle size and crystal orientation. Grinding produces pits whose basal area is of the order of magnitude of the cross-section area of the grinding particles. In the pits, there is a tendency for the cleavage planes (111) to be exposed. If the pits were simply formed by (111) planes, their depths would be in the order shown in the last line of Table I. (Only a range of values can be given for pits of this kind on the (111) surface because they may be truncated at any depth by the (111) plane parallel to the surface.) Pitting increases the etching rate by increasing the surface area. However, the rate will be modified by the particular faces present in the pits. As the crystal etches, the slow etching planes develop as pit faces in preference to the rapidly etching ones. For the (110) cut, the decrease in rate due to the development of slow etching faces in the pits ultimately dominates the increase due to area and results in the dip shown in Fig. 1. As etching progresses, the pits widen and grow shallower until their effect is negligible. The rate becomes a constant characteristic of the initial orientation of the sample and independent of previous surface history.

The thickness of the layer which must be removed before the etching rate becomes constant can be estimated from the curves of Fig. 2. Values of the range 2–10 μ are obtained. These are in the same range as the values for the thickness of the disordered layer reported by Faust (1) from life-time measurements and by Weissman (2) from x-ray line broadening studies. Clarke (3) has reported that the thickness of the disturbance which causes a change in the resistivity is an order of magnitude smaller (0.5 μ). This suggests that those properties of the lattice which affect lifetime and line width are disturbed to about the same depth as the surface is cracked and pitted. If this is true, the disturbed surface layer should be a function of crystal orientation and abrasive particle size. If the limit of the disturbance is arbitrarily defined as that depth at which the rate of etching has dropped to within 10% of its final value, the results are as shown in Table I.

Rate vs. Temperature for Various Orientations

The temperature dependence of the etching rate was measured for three crystal orientations. Data are plotted in Fig. 3, and it is seen that they do not lie on a simple straight line corresponding to a single activation energy. The points with the dots in the center were taken initially, while those with the crosses in the center are supplementary data taken with the same samples at a later date. The data are fitted approximately by pairs of straight lines which intersect at a knee in the vicinity of room temperature; the mean square deviation from these lines is about 5½%. The slopes of the lines give the approximate activation energies above and below room temperature as shown in Table II.

There are three particularly interesting features of these data: the change in order as the temperature is reduced, the knee occurring in all three curves at about room temperature, and the parallelism of the (110) and (111) curves.

At temperatures above 25°C, the rate is greatest for the (110) orientation and least for the (111) orientation. This order is in agreement with the order predicted some time ago from the etching of small germanium spheres (4). To check the reversal of order of the rates for the (100) and (111) surfaces at low temperatures, two adjacent samples were cut so that the (110), (111), and (100) surfaces were exposed. They were then ground identically and

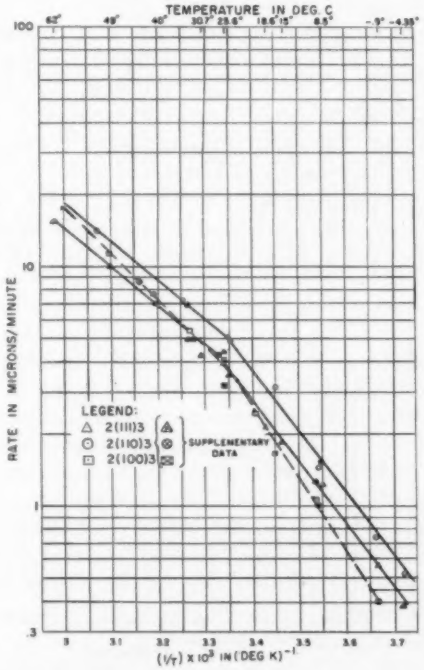

Fig. 3. Rate of etch vs. $1/T \times 10^3(°K)^{-1}$ for 3 crystal orientations. (No. 2 etch, 1 ohm-cm n-type germanium.)

TABLE II. *Activation energy in kilocal/mole*

Face	Above room temp		Below room temp	
	From slope	Fitting by eq. (I) (see below)	From slope	Fitting by eq. (I)
(100)	8.6	7	13.6	17
(110)	7.4	6	12.0	15
(111)	7.4	6	12.0	15

etched to remove the same amount of material. One was etched at 36.5°C, the other at 0°C, and the pit shapes compared. Characteristic pits were different and, assuming that the slow etching faces predominate in the pits, their shapes tended to confirm the rate data.

The question arises as to whether or not, on a microscopic scale, more than one crystal face etches. It seems evident that at least two different faces must etch, for Fig. 3 shows at least two orientation-dependent activation energies. Furthermore, if only two faces do etch, the measured rate should be a linear combination of these two rates. If only two faces etch and these are included in the group measured, the crystal geometry indicates that the rate for the third must be strongly affected by both. Thus, the reversal of order of the (100) and (111) at low temperatures becomes difficult to interpret. Apparently, therefore, if only two faces do etch, they are not any pair of the three studied.

The general shape of the rate vs. temperature curves cannot be accounted for either as the product or as the sum of terms of the form $A \exp(-E/kT)$. However, if the process is analyzed as a sequence of operations taking place on a limited surface, an equation is obtained which fits the data to within the limits of experimental error. The fact that the surface plays an important role is clear from the dependence on orientation over the whole temperature range.

Consider n reactions taking place consecutively on a surface. The rate of each process will be controlled not only by the temperature and concentration of the particular reactant involved, but also by the fraction of the surface available to that reaction. Thus,

$$R_j = a_j c_j^{p_j} f_j \exp(-E_j/kT)$$

where a_j = constant associated with reaction j; c_j = concentration of reactant involved in reaction j; p_j = power to which c_j enters reaction j; f_j = fraction of area available to reaction j; E_j = activation energy associated with reaction j. For the steady-state case, $R_1 = R_2 = \cdots R_j = \cdots R_n = R$ and by definition $f_1 + f_2 + \cdots f_j + \cdots f_n = 1$. Applying these two conditions and solving for the rate one obtains

$$R = 1 \Big/ \sum_1^n \frac{e^{E_j/kT}}{a_j c_j^{p_j}} \qquad \text{(I)}$$

For a surface reaction in which there are only two important rate-controlling processes, this reduces to

$$R = \frac{1}{\dfrac{\exp(E_1/kT)}{a_1 c_1^{p_1}} + \dfrac{\exp(E_2/kT)}{a_2 c_2^{p_2}}} \qquad \text{(II)}$$

Equation (II) correctly describes the observed rate temperature behavior over the range covered. For the (111) and (110) surfaces, this gives

E_1 6 kcal/mole $\quad a_1 c_1^{p_1}$ 1.41×10^5
E_2 15 kcal/mole $\quad a_2 c_2^{p_2}$ 8.48×10^{11}

and for the (100) surface it gives

E_1 7 kcal/mole $\quad a_1 c_1^{p_1}$ 7.50×10^5
E_2 17 kcal/mole $\quad a_2 c_2^{p_2}$ 2.37×10^{13}

Rate vs. Composition

Much of the published data on etching has stressed the importance of specific composition. A number of experiments were performed to learn how critical this dependence might be. From preliminary experiments, it had been supposed that the etching process proceeded by the oxidation of the germanium and the subsequent solution of the oxide. It was hoped that the composition experiments might also help in testing this interpretation.

If the etching process does proceed by oxidation and subsequent solution, it would be of interest to find out what one can about the oxidation process. If GeO is formed, then since this is insoluble, a second oxidation to GeO_2 very probably takes place. It can be seen from equation (I) that insight into these steps cannot be obtained from rate vs. concentration data taken at constant temperature. For if there are h successive reactions which involve the same reactant to the same power, then the form of the equation is identical to that in which these h reactions are replaced by only one. That is, the terms $1/a_1 c^p + 1/a_2 c^p \cdots 1/a_h c^p$ can be lumped together as 1/const. c^p. (The exponential term is a constant at a fixed temperature and is included in the a's.) Therefore, one cannot separate these h stages. Such a situation would arise if there were successive oxidations as proposed.

As the concentration of one reactant approaches zero, it is seen from equation (I) that

$$\lim_{c_j \to 0} \frac{\partial R}{\partial c_j} = \begin{cases} \infty & \text{if } p_j < 1 \\ a_j & \text{if } p_j = 1 \\ 0 & \text{if } p_j > 1 \end{cases}$$

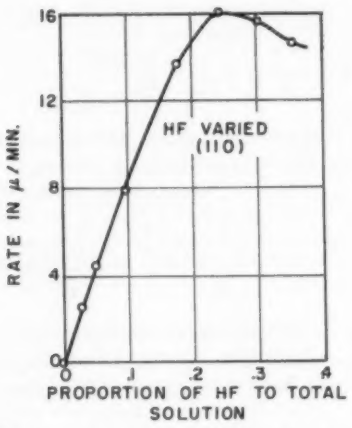

FIG. 4. Rate of etch vs. the ratio of the volume of reagent HF to total volume of solution.

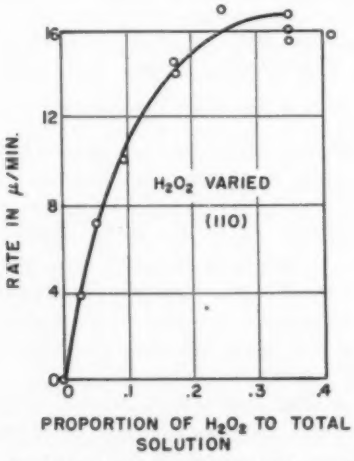

FIG. 5. Rate of etch vs. the ratio of the volume of reagent H_2O_2 to total volume of the solution.

Therefore, rate vs. concentration data should approach the origin asymptotically to the rate axis if $p_j < 1$, asymptotically to the concentration axis if $p_j > 1$, and with a finite slope if $p_j = 1$. From the measurements of rate vs. concentration for H_2O_2 and HF, Fig. 4 and 5, it appears that $p = 1$ for dilute solutions in each case. If the concentration of both the H_2O_2 and HF are varied simultaneously, as by simple dilution, the rate varies as shown in Fig. 6.

Fig. 7 shows the rate temperature behavior for several compositions. Curve (a) is for the standard composition, curve (b) for simple dilution, and curve (c) for a solution in which the concentration of the H_2O_2 has been reduced. The high temperature portions of all three curves have nearly the same slopes. The low temperature portions of (b) and (c) have the same slope, but this is different from that of (a). It is possible that when the rate is reduced sufficiently by reduction in the concentration of one or both of the reactants, a third limiting process (e.g., diffusion) begins to appear. In the light of equation (I), Fig. 7 might be interpreted to mean that both rate-controlling processes are dependent only on the concentration of the oxidizing agent, for example, the formation of a monoxide and then a further oxidation to a dioxide. In this case, energies obtained from the curve would be for successive oxidations. However, comparison of the rate vs. dilution data, Fig. 6, and the measurements of the rate as a function of the concentration of H_2O_2 and HF (Fig. 4 and 5) show that both the H_2O_2 and HF play rate-controlling roles over a wide range of concentrations. If the measured concen-

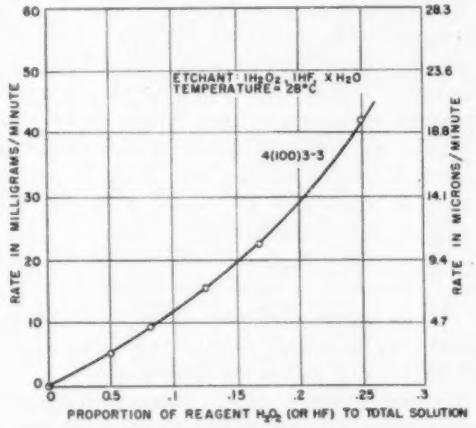
ETCHANT: 1 H_2O_2 : 1 HF : X H_2O
TEMPERATURE = 28°C
4(100)3-3
RATE IN MILLIGRAMS/MINUTE
RATE IN MICRONS/MINUTE
PROPORTION OF REAGENT H_2O_2 (OR HF) TO TOTAL SOLUTION

FIG. 6. Effect on etching rate of diluting etchant with water.

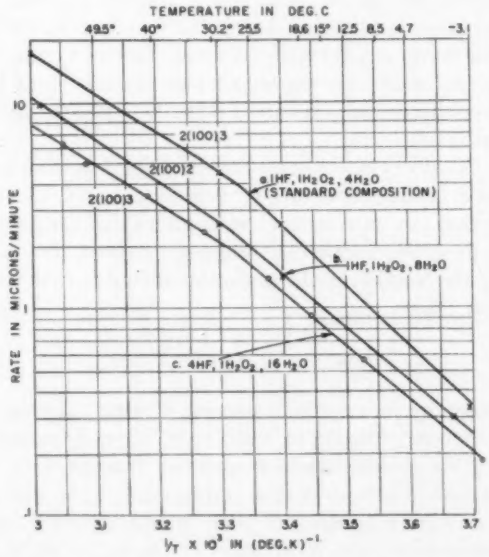

FIG. 7. Effect of etchant composition on rate vs. reciprocal temperature curves for samples in the (100) plane.

TABLE III. *Ratio of etching rates for 4-1-16 and 1-1-4 compositions of* HF-H_2O_2-H_2O *etchant*

$10^3/T$ °K	Relative etching rate	
	Calculated	Measured
3.7	0.7	0.6
3.3	0.38	0.46
3.0	0.33	0.48

trations are substituted into equation (I) (only c_1 and c_2 are changed), one obtains a new curve which should coincide with the experimental curve for the new composition. Calculated and experimental ratios relating the rates for a 4–1–16 (HF, H_2O_2, H_2O) composition to that of the standard 1–1–4 composition are given in Table III.

The agreement is not particularly good, but allowance has been made neither for dissociation in computing the new concentrations, nor for a third limiting process.

Using equation (I) to solve for the fractions, f_1, f_2, etc., one finds that $f_j = R/\dfrac{a_j c_j^{P_j}}{\exp E_j/kT}$. It becomes clear that, by varying the conditions, the fraction of the surface area covered with any particular reaction product may be varied. In this connection, it is worth mentioning a film which has been observed to form under conditions of reduced concentration of H_2O_2 (about 1 part pure H_2O_2 to 20 parts of total solution). It did not form during the etching or in distilled wash water. However, it did form immediately upon exposure of the freshly etched surface to air. The film is not soluble in water or in a 15% solution of HF in water. It is quickly removed by washing in a dilute H_2O_2 solution. It seems quite possible that the Ge is nearly bare when washed but that, on exposure to air, a monoxide layer forms. This is then fairly stable until oxidized to a dioxide by the H_2O_2. The dioxide is slightly soluble in water.

Rate vs. Impurity

To determine to what extent these results could be generalized to apply to other crystals differing in impurity content, measurements were made of the effect of varying the concentration of arsenic, the effect of changing the type of impurity, and the effect of thermally quenching a sample.

Fig. 8 is a plot of the temperature dependence of the etching rate of a 9.4 ohm-cm sample, (111) surface. Plotted on the same graph are the points for a 1 ohm-cm sample, (111) surface orientation, as a function of temperature, and data for (100) and (110) surfaces at one temperature. The single temperature points are the result of more than one observation. Close inspection of the results indicates that the 9 ohm-cm material etches slightly more rapidly than the 1 ohm-cm material. The difference is close to the estimated limit of experimental error, but appears to be reproducible. These samples were arsenic doped.

Further, more careful measurements have been made for all three orientations at room temperature. It was found that in each case the rate for 9 ohm-cm material was 7% greater than that for 1 ohm-cm material. Thus, somehow, four parts per hundred million of arsenic seem to inhibit the etching significantly. It is quite remarkable if one impurity atom on the surface masks 2.3 million germanium atoms or if the cross section for inhibition is 1.8×10^{-9} cm^2. It is significant also that somewhat incomplete data (Fig. 8) show this to be true over a wide range of temperatures. This offers a tempting subject for further study.

To find out if the rate of etching is strongly dependent on the type of impurity, samples containing vanadium (6 ohm-cm), antimony (2 ohm-cm), gallium and antimony balanced (0.7 ohm-cm), and indium (0.02 ohm-cm) were measured. All etched faster by about 10% than arsenic-doped material of 2 ohm-cm resistivity. However, control on the orientation was poor and these results are in doubt by perhaps 15%. At least no striking differences were

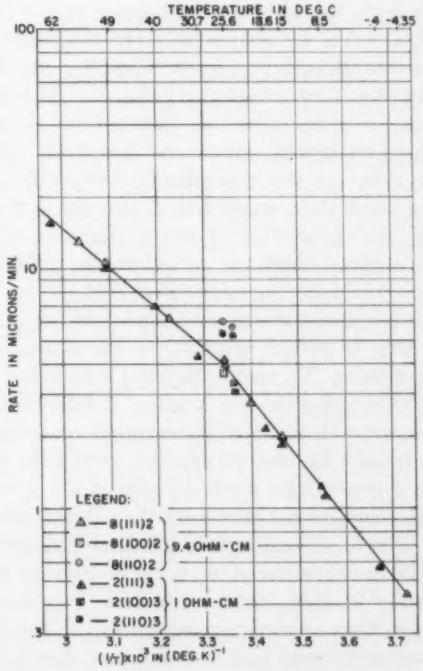

FIG. 8. Rate of etch vs. $1/T \times 10^3$(°K)$^{-1}$ for different resistivities (No. 2 etch).

observed. The best evidence to date that some impurities have a different effect on the etching rate than others came from the etching of small spheres. Spheres from crystals containing antimony and indium balanced (6 ohm-cm), phosphorus (0.1 ohm-cm), thallium (0.8 ohm-cm), and gallium (0.3 ohm-cm) were all etched to equilibrium form in the No. 2 etch. Of these, only the gallium-doped sample showed a marked difference from samples doped with arsenic. This difference was not great. For the gallium-doped sample alone, the equilibrium form was not a dodecahedron. This was an indication that the (110) plane was not the fastest etching plane. It appeared rather that a plane tilted very slightly away from the (110) toward the (100) etched most rapidly.

In order to find out quickly the effect of prior thermal treatment on the rate of etch, a simple experiment was tried. Two adjacent (100) slabs were cut from crystal T125N (n-type, 1 ohm-cm, arsenic doped). One of these was heated to a dull red heat in a gas-air flame for about a minute and then quenched by removal. This was repeated three times. The etching rate of the two samples was then compared at 21.8°C and found to be identical to better than the estimated error (2%).

Comparison of Etchants

Many different etchants are used in practice. Some of the most common are listed in the Appendix. The rate-vs.-temperature dependence of the No. 2, No. 3, and No. 4 etchants have been studied. Some results are plotted in Fig. 9. Data for the No. 3 etchant are very erratic and data for the No. 4 etchant are even worse, so that no curve can be drawn. Two of the points are completely off the graph. Some of the experiments performed in obtaining these data suggest that sometimes there is formed, on the surface of the germanium, a layer which acts to passivate or otherwise inhibit the reaction in these etchants. For example, a brief etch in No. 2 will make the sample almost immune for a time (a minute or more) to the action of the No. 3 etchant. No such inhibiting action has been observed in using the No. 2 alone. It follows that it may be desirable to use a concentrated version of the No. 2 etchant for the operations in which the No. 3 or No. 4 is normally used. An idea of the rates obtainable may be derived from the rate-vs.-dilution curve, Fig. 6. An undiluted mixture of reagent H_2O_2 and HF gives a rapid etch. If a dioxide forms ultimately in H_2O_2, then peroxide and pure water should etch germanium. An experiment to determine this was performed and it was found that a (111) surface is etched by 1 part 30% H_2O_2 in 5 parts water at 26°C at a rate of 0.0275 μ/min. This may constitute a useful slow etchant.

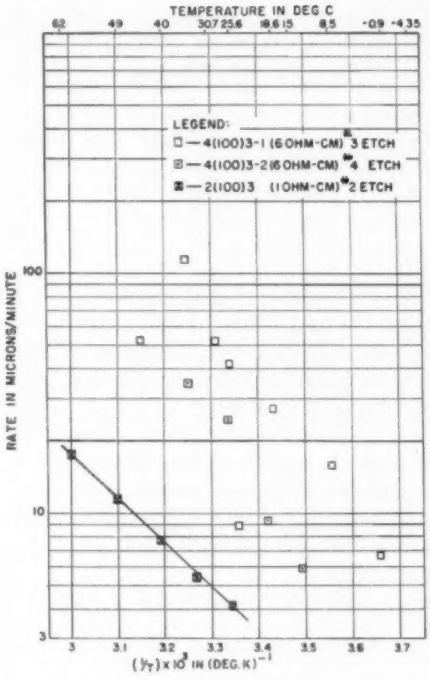
TEMPERATURE IN DEG C
62 49 40 30.7 25.6 18.6 15 8.5 -0.9 -4.35
LEGEND:
□ — 4(100)3-1 (6 OHM-CM) #3 ETCH
⊠ — 4(100)3-2(6 OHM-CM) #4 ETCH
▣ — 2(100)3 (1 OHM-CM) #2 ETCH
RATE IN MICRONS/MINUTE
100
10
3
3 3.1 3.2 3.3 3.4 3.5 3.6 3.7
(1/T) x 10³ IN (DEG. K)⁻¹

Fig. 9. Rate of etch vs. $1/T \times 10^3(°K)^{-1}$ for three different etchants. The erratic behavior of the No. 3 and No. 4 etchants makes it useless to draw curves through these data.

Conclusions

It has been found that an aqueous solution of HF and H_2O_2 is a reliable etchant for germanium. It is stable for long periods of time when stored in polyethylene and yields readily reproducible results for a wide range of temperatures and compositions when used under conditions of vigorous stirring. By suitably adjusting conditions, rates as low as 0.03 μ/min or as high as 20 μ/min may be obtained at room temperature. The etching rate is dependent on crystal orientation, surface disorder, and crystal impurity content, the rate being fastest for the (110) surface and pure germanium. The increase with surface disorder is comparable to the increase in surface area. The etching attack is apparently limited by two distinctly separate processes which take place in sequence on the surface of the crystal. Over the temperature range 0–60°C the rate of etching is found to obey an equation of the form

$$R = 1 \Big/ \sum_{1}^{n} \frac{e^{E_j/kT}}{a_j c_j^{P_j}}$$

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 Journal.

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APPENDIX

Composition of Commonly Used Germanium Etchants

H_2O_2 Technical Quality (Allied Chemical Co.) Assay 30–35%

HNO_3 Reagent Quality (Baker) Minimum Assay 69.2%

HF Reagent Quality (Allied Chemical Co.) Minimum Assay 48%

CH_3COOH Reagent Quality (Merck) Minimum Assay 99.8%

No. 2
- 1 part HF
- 1 part H_2O_2
- 4 parts H_2O

No. 3
- 56 cc HF
- 56 cc HNO_3
- 12.5 cc H_2O

No. 4
- 50 cc HNO_3
- 30 cc CH_3COOH
- 30 cc HF
- 0.6 cc Br

Electrokinetic Potentials of Bulk Metals by Streaming Current Measurements

I. Method[1]

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Defense Research Laboratory and Department of Chemistry, The University of Texas, Austin, Texas

ABSTRACT

A method for making a direct measurement of the streaming currents developed by fluid flow through metal capillaries is described, by means of which the electrokinetic (ζ) potentials of bulk metals can be determined. Experimental data proving the validity of the method are presented.

STREAMING POTENTIAL VS. STREAMING CURRENT

Although the electrokinetic phenomenon resulting from fluid flow through a capillary has been historically referred to by the expression "streaming potential," it is nevertheless a fact that the primary result of the fluid flow is a streaming *current*. The value of this current is given by the equation

$$I = \frac{\Delta P r^2 D \zeta}{4 \eta l} \qquad \text{(I)}$$

where ΔP is pressure drop across the capillary; r and l the capillary radius and length; D and η the dielectric constant and viscosity of the fluid; and ζ is the electrokinetic (or zeta) potential.

With but one exception, all previous measurements on this phenomenon have been made by placing measuring electrodes at the ends of the capillary and, by means of a potentiometer, applying just enough potential, E_s, to force an equal electrolytic current back through the center of the capillary (1). Since the electrolytic resistance R of the fluid inside the capillary is easily obtainable from the capillary dimensions and the conductivity k of the fluid, a direct relation between ζ and E_s is available, i.e.,

$$E_s = IR = \frac{\Delta P D \zeta}{4 \pi \eta k} \qquad \text{(II)}$$

The fact that investigations in this field have been restricted almost exclusively to measurements of the streaming potential is explained by the exceedingly low value of the streaming current, which is usually in the order of 10^{-10} to 10^{-11} amp. Instruments for measuring currents of this magnitude directly have not been available. On the other hand, the electrolytic resistance of the capillaries studied is often as high as 10^9 ohms, so that the values of streaming potentials obtained run into the hundreds of millivolts, a value easily and accurately measurable with a potentiometer. Furthermore, as long as the return current necessary to balance the streaming current could be forced to take a path of *known* resistance, there was no necessity for actually measuring the streaming current, as it could be obtained simply from Ohm's law. This has been precisely the case in almost all previous studies on this phenomenon, i.e., the materials used to form the capillaries have been nonconductors, so that the only path available for the return current has been the known electrolytic resistance back through the center of the capillary. The only appreciable trouble with potential measurements has been in determining the value of "surface conductance," a correction to the calculated electrolytic conductance which is necessary because the concentration of ions near the wall of the capillary is somewhat higher than that in the bulk of the liquid.

If now the nonconducting capillary wall is replaced by an electronic conductor, e.g., platinum, then measurements of streaming potentials as usually made are likely to be meaningless, or at best very difficult of interpretation, since the value of R can no longer be determined unequivocally. In this case, the path for the return current is a parallel circuit of three separate resistances, which are: (*a*) electrolytic resistance, R_1, which can be determined exactly; (*b*) resistance to conductivity along the surface, R_2, usually much larger than R_1, and which can be estimated with fair accuracy; and (*c*) resistance through the metal wall, R_3, which is itself composed of three parts (see below), only one of which can be determined.

It can be stated with reasonable certainty, however, that in most cases the values of R_1 and R_2 will be so very much larger than R_3 that they may be neglected entirely. Thus, for the largest diameter

[1] Manuscript received February 9, 1955.

capillary used in these experiments, the electrolytic resistance (R_1) with distilled water is calculated to be 1.2×10^9 ohms. Surface conductivity (through R_2) may decrease the total electrolytic resistance some 10%, so that these two parallel paths yield a resistance of some 10^9 ohms. Now, as shown below, even with all possible precautions taken to increase the value of R_3, it is still no larger than about 5×10^7 ohms. It remains, then, only to investigate the nature of R_3. In order for the return current, I, to flow through the capillary wall, it must: (*a*) enter at one end by means of an electrode reaction requiring a potential drop, E_1, (*b*) flow electronically through the metal wall causing an IR potential drop, and (*c*) return to the solution at the other end via another electrode reaction and an additional potential drop, E_2. Because of the very small values of I and of the electronic resistance of the capillary wall, the second term may be disregarded, and the measured streaming potential is then composed of the terms E_1 and E_2. Although there is very probably some relation between the streaming current and the potentials E_1 and E_2, it would be exceedingly difficult to determine, and would change radically from one system to another.

In view of the difficulties described above, it is apparent that any attempt to determine ζ-potentials by making streaming potential measurements on metal capillaries is foredoomed to failure. This was recognized by Kruyt and Oosterman (2), who attempted to make streaming potential measurements on platinum capillaries with no success. They explained the failure of their experiments by pointing out the existence of the lower resistance path through the metal. An earlier investigation by Zakrzewski (3) on silvered glass capillaries also yielded results which showed only that some type of electrical phenomena did result when a liquid was forced through a metal-walled capillary.

Basis of the Streaming Current Method

The solution to the problem of measuring the ζ-potential of bulk metals[2] lies in the use of an external measuring circuit with an electrical resistance so low that the bothersome shorting resistance of the capillary wall is itself shorted by a known resistance. Under these conditions, all the streaming current, except for a negligible fraction, must return through the external shunt. Preliminary investigations indicated that the value of the "apparent" resistance of the capillary is in the order of 10^6 to 10^7 ohms. An external measuring resistor of 10^4 ohms, then, should effectively shunt the capillary, so that measurements of the emf developed across the shunting resistor should give a true value for the streaming current. The applicability of this method was recognized earlier by Eversole and Boardman (4), in a study designed primarily to eliminate the effect of surface conductance. They pointed out, however, that use of this method should give true values of the streaming currents on metal capillaries, and reported results of measurements made on one platinum capillary. They were unable to short the capillary entirely, but used an extrapolation method to obtain the "true" value of the current. Use of the extrapolation method was necessary because instrumentation capable of measuring the low voltages developed by currents of 10^{-10} amp flowing through 10^4 ohm resistors (microvolts) had not at that time been perfected. The lowest value of external resistance they were able to use was 1.6×10^7 ohms, which is near the value of the capillary resistance itself. Recent advances in electronic circuitry have resulted in the development of extremely sensitive, yet stable, instruments for measuring voltages in the microvolt region. With these instruments it is possible to use the streaming method on metal capillaries, and thereby obtain a true value for the ζ-potential of bulk metals in contact with various liquids.

Circuit Analysis

The construction of the metal capillaries, pressure regulating system, and other experimental procedures, will be given in a subsequent paper, along with the results obtained on capillaries of three different metals (platinum, gold, and silver). The purpose of the present paper is simply to describe the method and demonstrate its validity.

Fig. 1 shows a line drawing of the electronic circuit and the fundamental parts of the fluid flow circuit. The streaming current was measured by recording the voltage drop across a ten thousand ohm resistor inserted into the external "shunting" circuit. This arrangement creates a closed circuit of two electrolysis cells in parallel, equivalent to the type shown in Fig. 2. Here A and B represent the measuring electrodes, C and D the ends of the capillary, and R the external resistor. The measuring electrodes are placed as near the capillary ends as possible so that electrolytic resistance through that part of the solution may be neglected. The solution contact through the capillary is not shown. The + and − signs indicate that ionic charge has been transferred through the capillary by fluid flow, and must now be returned by one or both of the two

[2] Potentials of metals have often been measured by using electrophoretic methods on metal sols. The validity of this method can also be questioned because of the conducting properties of the particles.

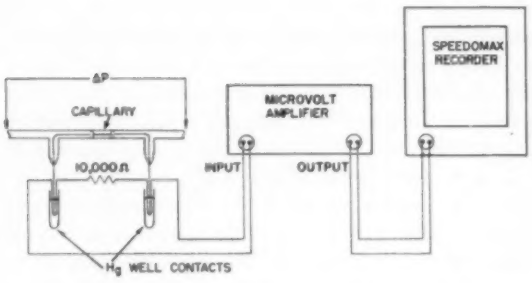

FIG. 1. Electronic circuit for streaming current measurements.

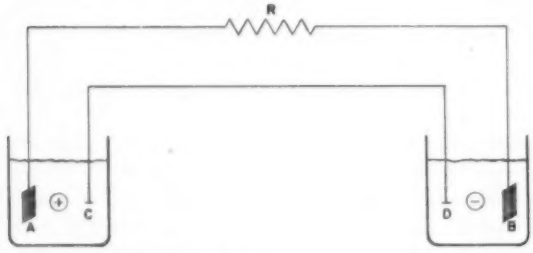

FIG. 2. Equivalent electrolysis cell. A and B are measuring electrodes, C and D are the capillary ends, R is the external resistor, + and − indicate transfer of charge by fluid flow.

circuits $A - B$ or $C - D$.[3] The potential drop through the measuring circuit is composed of three terms, viz.:

$$E_1 = E_A + I_1R + E_B . \qquad \text{(III)}$$

The potential drop through the capillary was shown earlier to be composed of two terms, which is written here as:

$$E_2 = E_C + E_D . \qquad \text{(IV)}$$

Since the circuits are in parallel, $E_1 = E_2$, and

$$E_A + I_1R + E_B = E_C + E_D . \qquad \text{(V)}$$

At low current densities, each of these E's may be replaced by a term kI/a (4), where a is the area of the electrode (or metal) exposed to the solution, I the current flowing into (or out of) the electrode, and k a "constant" of proportionality, so that equation (V) becomes

$$I_1\left[\frac{k_A}{a_A} + \frac{k_B}{a_B} + R\right] = I_2\left[\frac{k_c}{a_c} + \frac{k_D}{a_D}\right] \qquad \text{(VI)}$$

[3] As pointed out previously, the ionic resistance through the capillary is so large that it may be neglected as a return path.

and since $a_A \cong a_B$ and $a_C \cong a_D$, then

$$\frac{I_1}{I_2} = \frac{\left[\dfrac{k_C + k_D}{a_{CD}}\right]}{\left[\dfrac{k_A + k_B}{a_{AB}} + R\right]} \qquad \text{(VII)}$$

Although the values of the k's in this equation are not known, it is possible to show that the ratio I_1/I_2 can be made so large that the value of I_1 truly represents the streaming current.

If the value of R is much less than the quantity $[k_A + k_B]/a_{AB}$, equation (VII) reduces to:

$$\frac{I_1}{I_2} = \left[\frac{k_C + k_D}{k_A + k_B}\right]\left[\frac{a_{AB}}{a_{CD}}\right] \qquad \text{(VIII)}$$

which means that small changes in R (doubling, tripling, etc.) should not affect the measured quantity, I_1. However, if R is much larger than $[k_A +$

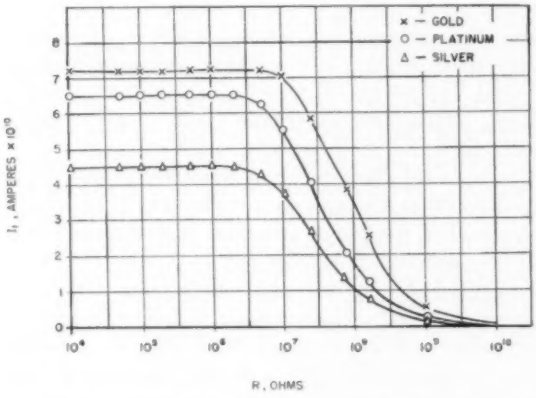

FIG. 3. Current in the external circuit as a function of the external resistance.

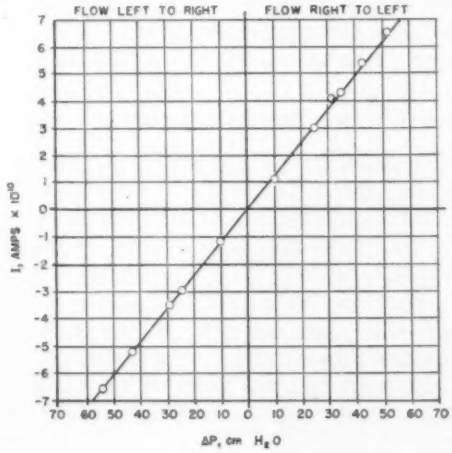

FIG. 4. Pressure-current curve for the 0.0138 x 1.724 cm gold capillary in distilled water.

$k_B]/a_{AB}$, then equation (VII) becomes

$$\frac{I_1}{I_2} = \frac{k_C + k_D}{a_{CD}R} = \frac{k'}{R} \qquad \text{(IX)}$$

and small changes in R will be immediately reflected in I_1. Furthermore, if equation (VIII) applies when $R = 10{,}000$ ohms, it is possible to increase the value of R until equation (IX) applies, at which point I_1 will begin to decrease, and with still larger values of R it will approach zero asymptotically. This experiment was carried out with distilled water (conductivity $< 2.0 \times 10^{-6}$) and capillaries of each of the three metals, and gave the results shown in Fig. 3. A similar curve was obtained when the measuring electrodes were removed further and further from the ends of the capillary, with no decrease in I_1 noted until the electrodes were some 10 cm removed. It is apparent from the figure that, for values of R less than 10^6 ohms, equation (VIII) applies, and that I_2 is negligibly small. For the platinum capillary, since the measuring electrodes are also platinum, $k_A + k_B$ is approximately equal to $k_C + k_D$, so that the currents will split according to the ratio of the areas a_{AB}/a_{CD}. The results shown in Fig. 3 indicate that this is also true for the gold and silver capillaries. For this reason, the capillaries were constructed so that as little metal as possible (a_{CD}) would be exposed to the solution. With a_{CD} small, increasing a_{AB}, as by platinizing, had no measurable effect on the current I_1.

The potential drop across the 10,000 ohm resistor was amplified by means of a L&N Model 9825-B microvolt amplifier, and then fed into a L&N Model "G" Speedomax recorder. This combination results in a recording millimicro-ammeter with an internal resistance of 10,000 ohms. Current readings were easily reproducible to within 1%, and held steady for long periods of time (>5 min). The ζ-potential was calculated from the equation

$$\zeta = \left[\frac{4\eta}{D}\right]\left[\frac{l}{r^2}\right]\left[\frac{I}{\Delta P}\right] \qquad \text{(X)}$$

which was obtained upon rearranging equation (I). Measured values of I were plotted against the applied pressure, the slope of this line giving the quantity $[I/\Delta P]$. A typical plot is shown in Fig. 4. Measurements were made on platinum, gold, and silver capillaries in contact with distilled water and dilute aqueous electrolytes; results of these measurements will be presented in a second paper.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Impedance Measurements at Solid Electrodes in Molten Lithium Chloride-Potassium Chloride[1]

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ABSTRACT

Impedance measurements have been made at solid microelectrodes in molten potassium-lithium chloride eutectic, and in dilute solutions of platinum(II), nickel(II), and cobalt(II) in the eutectic as a solvent. Capacitance and resistance measurements are described for forward (cathodic) polarization of a platinum microelectrode and for reverse polarization of the plated microelectrode. The results are interpreted in the light of a theoretical interpretation of pseudocapacity.

Introduction

Impedance measurements at microelectrodes have been used to obtain information relating to the kinetics of electrode reactions occurring at the microelectrode surface. The theories involved have been developed by several authors, especially Randles (1), Grahame (2), Ershler (3), and Gerischer (4). Generally, these techniques have found most application to reactions in aqueous solutions using dropping mercury electrodes. Ershler (3) and Hillson (5) have developed the theory for a metal electrode in equilibrium with its ions.

The normal procedures used in obtaining the needed measurements are as follows. An a-c bridge is used to measure a gross series or parallel resistance-capacitance combination. The solution resistance is measured in the presence of the excess supporting electrolyte which must be used and before any reducible species are added. The double layer capacity is measured as a function of potential in a solution of the supporting electrolyte. Measurements of the gross resistive-capacitative components are then made with the reacting species present. For rate constant determinations, this is usually done at the null potential, generally by having equal concentrations of the reduced and oxidized form in solution, or, for metal deposition, using a mercury amalgam of the same concentrations as the reducible metal ion in solution. Where a solid metal electrode is used, as in the study of copper deposition by Hillson (5), the use of a large copper reference electrode and copper microelectrode places the system at its null potential. From these measurements, it is possible to separate vectorially the gross measurements into the separate components (1, 6). The expressions for the pseudocapacity and polarization resistance as applied to a case of a solid electrode, where the diffusing oxidized species is reduced to the metal which deposits on the electrode, are (4, 5, 7):

$$R_r = \frac{RT}{n^2\mathbf{F}^2AC}\left(\sqrt{\frac{1}{2\omega D}} + \frac{1}{k}\right) \qquad \text{(I)}$$

$$C_r = \frac{n^2\mathbf{F}^2AC}{RT}\sqrt{\frac{2D}{\omega}} \qquad \text{(II)}$$

$$R_r - \frac{1}{\omega C_r} = \frac{RT}{n^2\mathbf{F}^2AC}\frac{1}{k} \qquad \text{(III)}$$

Where R, T, n, and $\mathbf{F}$ have their usual significance, C is the concentration of the oxidized form in solution, A the area of the electrode, D the diffusion coefficient of the diffusing oxidized form, k the heterogeneous rate constant defining the rates of the opposing dissolution and deposition reactions at the equilibrium potential as kC moles per second per unit of area of electrode surface, and ω being 2π times the frequency of the small a-c bridge signal. Thus, according to the theory, if the polarization resistance and the impedance due to the pseudocapacity are plotted against the reciprocal of the square root of frequency, two parallel straight lines should be obtained and the separation between the two straight lines is related to the rate constant k by equation (III).

The more general technique of Grahame (2) consists of applying a d-c base potential, on which is impressed the small (10 mv or less) a-c bridge signal. In this manner, a plot of the resistive and capacitative component due to the electrode reaction against the applied d-c potential is obtained. For reversible reactions occurring at the dropping mercury electrode, Grahame has shown that the impedance reaches a minimum at the polarographic half-wave potential and that, as the rate of the

[1] Manuscript received January 24, 1955. This paper was prepared for delivery before the Cincinnati Meeting, May 1 to 5, 1955, and was abstracted from the Ph.D. thesis of R. A. Osteryoung, University of Illinois, 1954.

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reaction decreases, that is, it becomes less reversible, the extent of the minimum in the impedance-d-c potential curve lessens and gradually shifts away from the reversible half-wave potential.

For the case of a single diffusing species, such as an infinitely rapid reversible metal-metal ion electrode, the impedance should be inversely proportional to the slope of the c.-v. curve (7), and should approach infinity with cathodic polarization as the diffusion-limited plateau is approached. With anodic polarization, no plateau is approached, and the impedance should approach zero.

In the present work, impedance measurement techniques were applied to dilute solutions of platinum(II), nickel(II), and cobalt(II) in a lithium chloride-potassium chloride eutectic melt at a temperature of 425° ± 10°C, using platinum electrodes.

Experimental

Fig. 1 is a diagram of the a-c bridge used in this work. The signal generator was a Heathkit Audio Generator, the output of which was fed into the bridge through the shielded audio transformer, T, which was a 4:1 stepdown transformer. The output of the signal generator was set at 40 mv; this coupled to the bridge through the transformer meant a 10 mv applied alternating signal. R_1 and R_p were Leeds & Northrup decade resistance boxes. C_p was a General Radio precision decade capacitor, which was wrapped in copper screening to reduce stray pickup. C_1 was a General Radio 1.0 μf precision mica capacitor. The potentiometer was a Leeds & Northrup student type. R_2 was a 0–0.5 megohm wire wound resistor, which led to the positive lead of the Sargent "Ampot." The amplifier was a Heathkit WA P-2 audio amplifier. The high voltage to the amplifier was supplied by a Heathkit variable Voltage Regulated Power Supply. The filament supply was a 6 v lead storage battery. A 304H du Mont Cathode Ray Oscilloscope was used.

The cell was a Pyrex glass tube, 13 in. long, 40 mm in diameter with a side arm of 9 mm tubing attached to a vacuum pump. The electrodes were inserted into holes in a No. 9 rubber stopper. The microelectrode was made of B. and S. gauge No. 26 platinum wire sealed into 6 or 8 mm tubing. The exposed length was approximately 1 mm. The two foil electrodes were hammer-welded to platinum wire. They had a surface area greater than 2 cm^2.

The cell was filled with 100–120 g KCl-LiCl eutectic mixture, and a solid rubber stopper was placed in the opening. The mixture was fused under vacuum and allowed to remain under vacuum overnight. Air was then admitted, the solid stopper removed, and the stopper with the electrodes inserted. Small amounts of reducible material could be added by removing the electrodes and dropping the desired material down a large glass tube which served as a funnel.

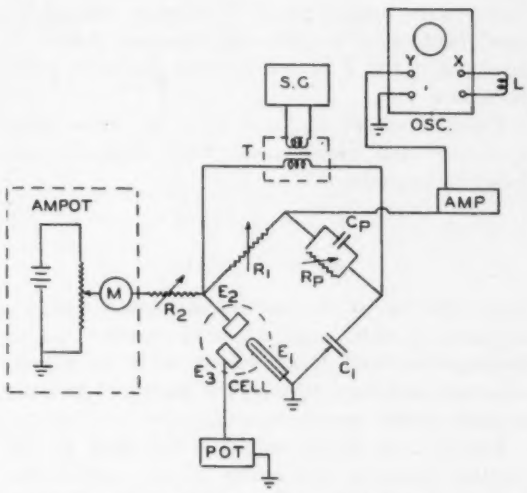

Fig. 1. Impedance bridge. S.G.—Heathkit audio generator; Pot.—student-type potentiometer; Ampot—E. H. Sargent and Co.; R_1, R_p—0–11, 110 ohm variable decade resistors; C_p—0–1.110 μf variable capacitor; C_1—1.00 microfarad capacitor; R_2—500,000 ohm variable resistor; Amp—Heathkit WA-P2 audio amplifier; Osc—du Mont cathode ray oscillograph; T—4:1 stepdown shielded audio transformer; L—60 cycle pickup loop; E_1—platinum microelectrode; E_2—platinum foil working electrode; E_3—platinum foil reference electrode.

To determine if the bridge was operating properly a decade resistor and capacitor were connected in series in place of the cell and measurements made at various frequencies.

By means of the Ampot, a d-c potential could be applied across the microelectrode, E_1, and the working platinum foil, E_2. The potential at E_1 was measured with respect to the platinum foil E_3, using the potentiometer. R_2 served to prevent shorting the a-c signal. By having the balancing resistor, R_p, and capacitor, C_p, in parallel, the impedance of the cell appeared as a resistance and capacitance in series (8). The impedance measured is that associated with the microelectrode, since any impedance due to the large electrode would be in series with that of the microelectrode, and would be much smaller than that of the microelectrode. With R_1 adjusted to a suitable value, a potential was applied with the Ampot. The off balance a-c signal was fed through the amplifier to the Y plates of the oscilloscope. A loop of wire attached to the X plates of the oscilloscope served to pick up a 60-cycle signal. The result on the oscilloscope face was a pulsating Lissajou figure. By adjusting R_p and C_p, pulsations were brought to a minimum, which was

taken as the balance point. This type of balance was used because of considerable 60-cycle pickup introduced to the Y plates from the electrodes in the furnace.

Calculations of R_{xs} and C_{xs}, the gross series resistance and capacitance, were made by the following formulas (8):

$$C_{xs} = (R_p/R_1)C_1$$

$$R_{xs} = (C_p/C_1)R_1$$

The advantage of the parallel measuring circuit is apparent in that large values of capacity can be measured without the necessity of using a large standard capacitor. Rather, the measured capacity depends on the ratio of R_p to R_1.

Curves were run by applying the fixed d-c potential, balancing the bridge at the desired frequency setting, then changing the d-c potential and again balancing.

As the d-c potential was increased, an electron current began to flow from ground to E_1, through E_2 to the resistance R_2, through the Ampot, where the meter, M, measured the current, then back to ground. Thus, a plot of the current behavior as the potential was changed could be obtained at the same time as the impedance. Residual current did not affect impedance measurements. Since the maximum potential output of the Ampot was only 3 v, it was necessary to lower the resistance of R_2 if currents greater than 4 μa were to pass. The effect of lowering R_2 was to increase the potential across E_1 and E_2.

The result of changing the d-c potential, with a reducible ion in the melt, was to deposit the metal on the platinum microelectrode. By then reversing the direction of polarization, the current-voltage curve was retraced, except that the curve crossed the zero current axis because of the oxidation of the metal deposited on the microelectrode. By changing the d-c potential, a larger and larger anodic current could be drawn. This current, of course, was not diffusion limited as was the reduction current. Thus, the combination of the ammeter, M, and the potentiometer gave a current-voltage curve and the bridge could be balanced at fixed microelectrode potentials and fixed anodic currents.

An equilibrium potential, that is, the potential of the metal plated microelectrode with respect to the reference platinum foil, could be measured by opening the direct current path through resistor R_2 and measuring the open circuit potential between E_1 and E_3.

Results

The results of the experiments are best presented in a series of graphs. The conditions under which

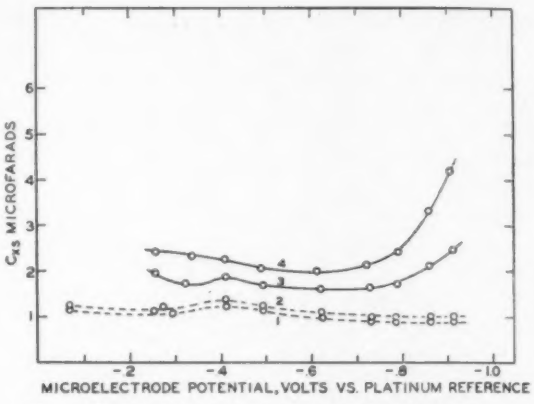

FIG. 2. Residual capacity, C_{xs} for KCl-LiCl. Curve 1, 2000 cps; curve 2, 1000 cps; curve 3, 100 cps; curve 4, 40 cps.

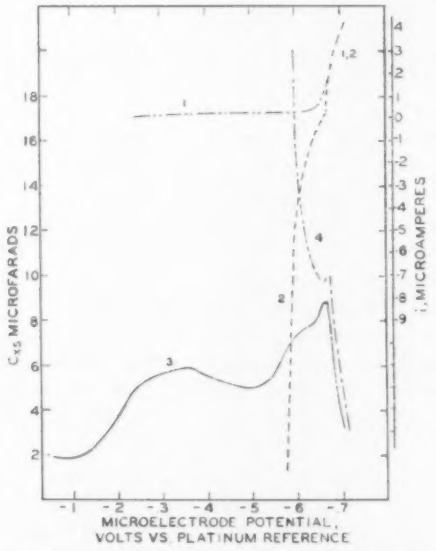

FIG. 3. C_{xs} and current for $NiCl_2$ (29 mg) in KCl-LiCl (113 g); f = 1000 cps. Curve 1, current, forward polarization; curve 2, current, reverse polarization; curve 3, C_{xs}, forward polarization; curve 4, C_{xs}, reverse polarization.

the experiments were run are presented on the graphs. Since the area of the solid microelectrodes was not known exactly, values of C_{xs} and R_{xs} are presented for the microelectrode used, rather than being expressed as microfarads per square centimeter or ohm cm^2.

Fig. 2 shows the residual value for C_{xs}, that is, the value obtained for the capacity of the measured series circuit without any reducible ions added. At the more negative potentials, a small residual current, due to the reduction of hydrogen from traces of water or hydroxyl ion in the melt, was drawn.

The graphs for C_{xs}, R_{xs}, and i, the current at the microelectrode, are plotted against the potential

measured with respect to the platinum foil reference electrode for the forward polarization for melts containing nickel ions, Fig. 3, and cobalt ions, Fig. 4. It is observed that the maximum in the value for C_{xs} and minimum for R_{xs} occur at the measured equilibrium potential. For the reverse polarization, Fig. 3 and 5, it is seen that the curves retrace that for the forward polarization until the maximum or minimum is reached, then show a slight jog, after which C_{xs} continues to increase and R_{xs} to decrease as the current becomes more and more anodic. Note that the jog in the current-voltage curve corresponds to the jog in the C_{xs} and R_{xs} plots. Fig. 6 shows the effect of frequency variation on C_{xs} for nickel ions in the melt. The effect of concentration changes of the reducing species is shown in Fig. 7. It is observed that the shift in the maximum in C_{xs} and minimum in R_{xs} corresponds to the shift in the equilibrium potential. The abnormally large shift in equilibrium potential is probably attributable to a drift in the potential of the reference electrode.

Fig. 8 shows a plot of C_{xs}, R_{xs}, and i against the microelectrode potential for the forward and reverse polarization with potassium tetrachloroplatinate(II) present in the melt. In this case, zero volts against the platinum reference corresponds to the equilibrium potential. In Fig. 9, values of C_{xs} are plotted against the reciprocal of the square root of the frequency for varying values of anodic current with the tetrachloroplatinate(II) present in the melt.

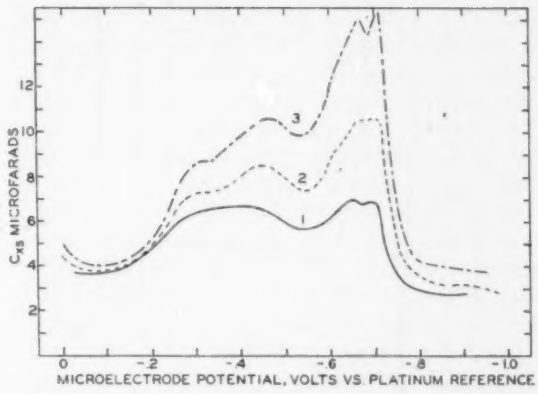

FIG. 6. C_{xs} for $NiCl_2$ (ca 30 mg) in KCl-LiCl (ca 100 g). Forward polarization, null potential = −0.68 v. Curve 1, 1000 cps; curve 2, 200 cps; curve 3, 100 cps.

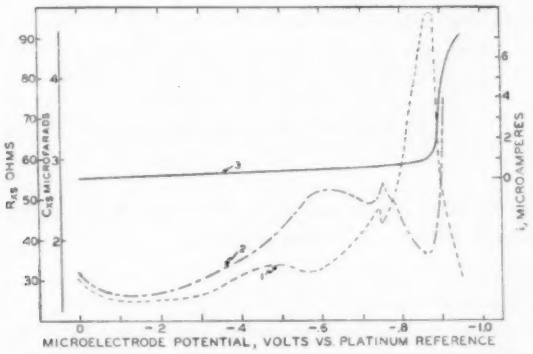

FIG. 4. C_{xs}, R_{xs}, and current for $CoCl_2$ (22 mg) in KCl-LiCl (106 g) forward polarization, null potential = −0.85 v.; f = 1000 cps. Curve 1, C_{xs}; curve 2, R_{xs}; curve 3, current.

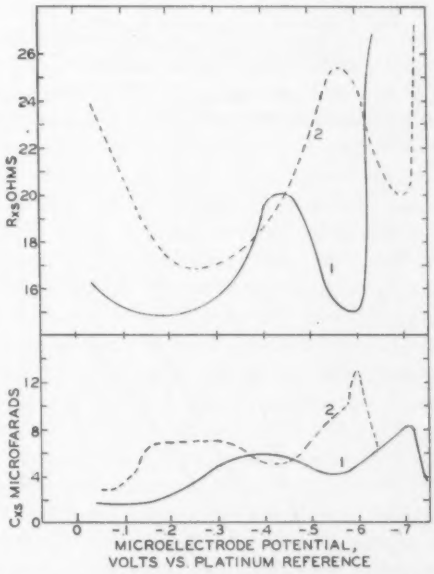

FIG. 7. C_{xs} and R_{xs} for $NiCl_2$ in KCl-LiCl; f = 1000 cps. Curve 1, 29 mg; curve 2, 54 mg $NiCl_2$ in 112 g KCl-LiCl.

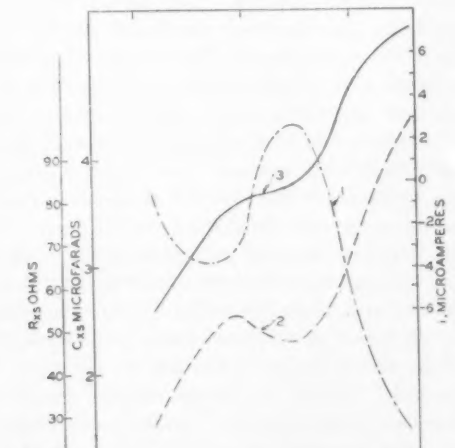

FIG. 5. C_{xs}, R_{xs}, and current for $CoCl_2$ (22 mg) in KCl-LiCl (106 g) reverse polarization, null potential = −0.85 v; f = 1000 cps. Curve 1, C_{xs}; curve 2, R_{xs}; curve 3, current.

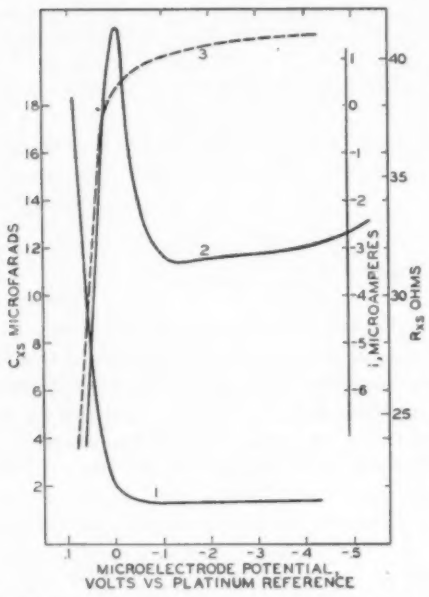

FIG. 8. C_{xs}, R_{xs}, and current for K_2PfCl_4 (27 mg) in KCl-LiCl (113 g); f = 1000 cps. Curve 1, C_{xs}; curve 2, R_{xs}; curve 3, current.

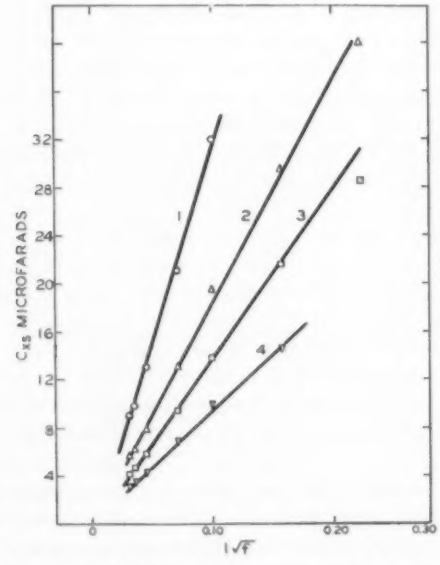

FIG. 9. C_{xs} as function of frequency, for K_2PfCl_6 (27 mg) in KCl-LiCl (113 g) at various values of anodic current. Curve 1, i = −4; curve 2, i = −1.5; curve 3, i = −0.5; curve 4, i = 0 μa.

The total measured impedance,

$$Z = \sqrt{(1/\omega C_{xs})^2 + R^2_{xs}}$$

for the electrode in a melt containing nickel(II) ions, is shown in Fig. 10 for the forward polarization.

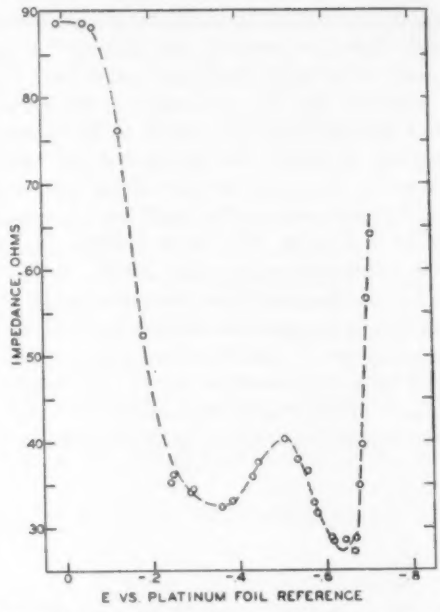

FIG. 10. Electrode impedance as function of potential, for $NiCl_2$ (29 mg) in KCl-LiCl (113 g), f = 1000 cps.

Note that the minimum in the impedance curve occurs at the equilibrium potential.

DISCUSSION

When impedance measurements are made in aqueous solutions using the dropping mercury electrode, the solution resistance and double layer capacity are measured and are found to be frequency independent. However, as indicated in Fig. 2, the "residual" capacity and resistance are not frequency independent. This has been attributed to the non-homogeneous character of the surface of a solid microelectrode (2, 9). Hillson (5) has suggested that a measurement of the double layer capacity at a solid electrode could be made by plotting C_{xs} against the reciprocal of frequency, and extrapolating to infinite frequency. The solution resistance might also be measured in a similar manner. However, the residual current in fused salt polarography, or in aqueous polarography employing solid electrodes, is a faradaic current, while the residual current obtained with a dropping mercury electrode is nonfaradaic, caused by the charging of the double layer at the continuously forming electrode-solution interface. The faradaic residual current would probably contribute some frequency dependent character to any resistance or capacity measurements, especially at lower frequencies. Thus, even if the values of C_{xs} and R_{xs} were extrapolated to a value at infinite frequency, the use of these values might lead to

serious error, since it would be used in a case where the frequency dependent component arises from the residual reaction plus that of the primary reaction being studied.

Attempts to calculate R_r and $1/\omega C_r$, equations (I) and (II), by subtracting vectorially the measured residual resistance and capacitance at a given frequency, were unsuccessful, leading to nonlinear and "inverted" plots against $1/\omega^{-1/2}$ in which the resistive component was less than the capacitative component of the impedance. A similar inversion was observed in plotting the uncorrected R_{xs} and $1/\omega C_{xs}$ values. Such an inverted behavior has been attributed to adsorption of the reacting species at the electrode surface (6). Unfortunately, there is no independent indication of adsorption in the present instance, although such a process is certainly possible. An adsorbed layer of reacting ions would lead to another (frequency independent) combination of resistance and capacitance across the double layer.

The resulting complexity of the impedance network, particularly in view of the abnormal frequency dependence of the double layer capacity and solution resistance, renders a quantitative interpretation impossible. Nevertheless, certain gross effects may be noted from the raw C_{xs} and R_{xs} plots.

For platinum(II), the current-voltage curve and C_{xs} conform closely to the expected behavior for a reversible couple. As shown in Fig. 9, the values of C_{xs} plotted against the reciprocal of the square root of frequency do fall reasonably well on a straight line, showing that the major portion of the impedance shows the proper frequency dependence. The pseudocapacity, C_r, is proportional to the slope of the current-voltage curve, di/dE, which in turn is proportional to the quantity $(i_d - i)$. In Fig. 9, the slopes of the curves, neglecting double layer capacity, should thus be proportional to $(i_d - i)$. Taking $i_d = 1.5$ μa, the calculated ratios of the slopes to the value of $(i_d - i)$ are respectively 2.5, 2.7, 2.7, and 2.2 for $i = 0$, -0.5, -1.5, and -4 μa. It follows from these observations that the observed pseudocapacity at a given potential (not the equilibrium potential) for a *reversible* electrode should be independent of the bulk concentration of the metal ion, because the surface concentration is determined by the electrode potential and the pseudocapacity measurement is not affected by the passage of a direct current. An unexpected irregularity is the crease of R_{xs} with cathodic polarization (Fig. 8). It has already been pointed out that R_{xs} is abnormal, perhaps due to adsorption.

For nickel(II) (Fig. 3) and cobalt(II) (Fig. 5), the current-voltage curves show increasing deviation from reversible behavior. As the reaction rate kC at the equilibrium potential decreases in relation to the diffusion flux, the current-voltage curve shows a region of diminished slope in the vicinity of the zero current point. Correspondingly, the value of C_{xs} does not increase smoothly in passing through the zero current point toward anodic polarization, as would be the case for a strictly reversible reaction. Actually, the jog is barely noticeable in the case of nickel(II), and the electrode reaction normally would be considered to be reversible by polarographic standards (10). By equilibrium potential methods, even the cobalt reaction probably would show reversible Nernst behavior, but its polarographic behavior is irreversible (11).

An unexpected but very striking observation was the increase in measured capacity C_{xs} which was observed on cathodic polarization of a platinum electrode in solutions of nickel(II) and cobalt(II) at potentials well before the equilibrium potential was reached. The strong frequency dependence of the capacity (Fig. 6) suggests that the diffusing metal ion is involved. The total impedance (Fig. 10) is considerably smaller in the potential region -0.2 to -0.6 v than in the absence of nickel(II) ion. Moreover, in blank experiments using the LiCl-KCl melt, a steady increase of total impedance with cathodic polarization was observed in this region, whereas two pronounced dips occurred in the presence of the nickel(II). No corresponding changes of slope in the current voltage curve were detected. This would appear to indicate that the peculiar impedance effects were not caused by residual electrode reactions in the blank melt.

The expected behavior would be to find only the double layer capacity at potentials more positive than the equilibrium potential of the plated metal. A pseudocapacity suddenly should appear at the reversible potential, and gradually decrease with increasing cathodic potential.

Since the pseudocapacity depends on the occurrence of the reaction

$$Mn^+ + ne \rightarrow M$$

and since there should not be any metal deposited on the inert electrode before the equilibrium potential, the possibility of metal deposition before the equilibrium potential must be considered. Rogers has shown that, in very dilute aqueous solutions, a deposition of silver of less than a monolayer takes place at a potential more positive than that predicted by the Nernst equation (12–14). Although further proof would be needed to establish the existence of such a deposit in the fused salt melt, such behavior might explain why the pseudocapacity,

although reaching a maximum at the equilibrium potential on the forward polarization, does start to increase well before the equilibrium potential.

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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Technical Note

The Nature of Aluminum as a Cathode[1]

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During the course of an investigation of galvanic corrosion, it was observed that aluminum, copper, and mild steel exhibited markedly different cathodic polarization curves in sodium chloride solution.

The results of this preliminary investigation are summarized in Fig. 1 which shows cathodic polarization curves for cold rolled aluminum[2] etched in ½% hydrofluoric acid, mild steel etched in 2% nital, and copper etched in 1:1 nitric acid. After etching, all specimens were stored in dry air for 24 hr to permit the growth of air-formed oxide films. The curves were determined in normal sodium chloride at 25° ± 0.1°C on specimens having an area of 100 cm² and probably represent continuations of the local-cell cathodic polarization[3] curves.

In the absence of an applied current, corrosion of iron (1), copper (2), and aluminum (3) in sodium chloride solutions involves the consumption of dissolved oxygen. The reduction of dissolved oxygen at iron and copper cathodes results in the formation of water or hydroxyl ions (4). Hydrogen peroxide may be formed transiently as an intermediate product of reduction (5), but will be rapidly catalytically decomposed by these two metals (4). Whether detectable quantities of hydrogen peroxide are formed at aluminum cathodes has been the subject of much argument (4, 6, 7) over the years. However, if hydrogen peroxide were formed as the cathodic reaction product during the corrosion of aluminum, this alone would not explain the very high cathodic polarization shown in Fig. 1 since this polarization is observed not only at low currents where oxygen is reduced but also at higher currents where hydrogen is evolved.

Cathodic reactions on these metals presumably occurred by the migration of electrons through the surface oxide films and the subsequent interaction of these electrons with hydrogen ions and dissolved oxygen at the film/solution interfaces. In order for this reaction to occur over most of a specimen, oxide films should have a low electronic resistance. The

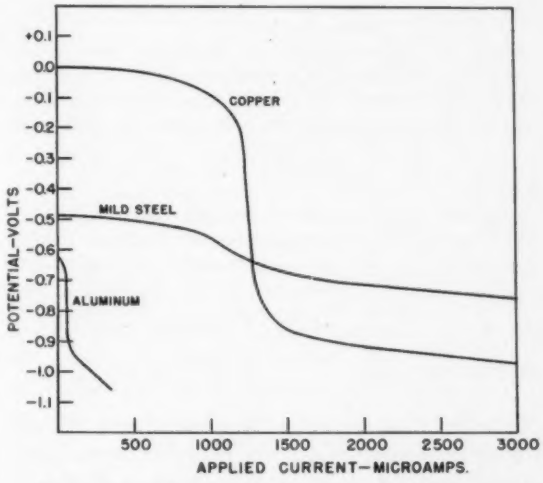

Fig. 1. Cathodic polarization curves for aluminum, mild steel, and copper in 1*N* sodium chloride solution at 25°C.

TABLE I. *Chemical compositions of the metals used*

Metal	Composition
Aluminum	Silicon 0.001%, iron 0.001%, copper 0.002%, balance aluminum.
Mild steel	Carbon 0.07%, silicon 0.02%, manganese 0.45%, phosphorus 0.010%, sulfur 0.030%, copper 0.06%, nickel 0.08%, molybdenum 0.005%, cobalt 0.03%, balance iron.
Iron	Carbon 0.005%, silicon 0.0075%, sulfur 0.013%, phosphorus 0.003%, manganese 0.007%, nickel 0.018%, chromium 0.02%, copper 0.003%, oxygen 0.12%, nitrogen 0.008%, hydrogen 0.00009%, balance iron.
Copper	Silicon 0.002%, iron 0.002%, magnesium <0.001%, silver <0.001%, oxygen 0.085%, balance copper.
Magnesium	Silicon 0.09%, iron 0.006%, magnanese 1.69%, copper 0.004%, zinc 0.08%, balance magnesium.
Zinc	Silicon 0.08%, iron 0.001%, magnesium 0.008%, copper 0.009%, lead 0.002%, calcium 0.002%, balance zinc.
Tin	Silicon 0.06%, iron 0.005%, magnesium 0.02%, copper 0.005%, lead 0.002%, calcium 0.004%, balance tin.
Lead	Silicon 0.1%, iron 0.0005%, magnesium 0.03%, copper 0.03%, balance lead.

[1] Manuscript received February 21, 1955.

[2] *See* Table I for chemical compositions.

[3] All potentials are expressed on the Standard Hydrogen Scale.

TABLE II. *Results of tests for cathodic areas on metals*

Metal	Phenolphthalein test for alkalinity	Cupric sulfate test for distribution of deposited copper	Sodium molybdate test for hydrogen peroxide
Iron	Development of alkalinity over whole specimen.	Uniform layer of copper deposited over entire specimen (Fig. 2*a*).	—
Copper	Development of alkalinity over whole specimen.	Uniform layer of copper deposited over entire specimen (Fig. 2*a*).	—
Magnesium	Development of alkalinity over whole specimen.	Loose deposit of copper formed over most of the surface; however, vigorous evolution of hydrogen continually detaches the copper.	—
Tin	Development of alkalinity over whole specimen.	Uniform layer of copper deposited over entire specimen.	—
Lead	Development of alkalinity over whole specimen.	Uniform layer of copper deposited over entire specimen.	—
Zinc	Only very slight pink color developed within the current range 0.5–2.5 microamp/cm^2. Above 2.5 microamp/cm^2 alkalinity is developed over the whole surface.	Uniform layer of copper deposited over entire specimen.	Uniform reddish-brown coloration over most of the surface.
Aluminum	No alkalinity detected when the current is less than 20 microamp/cm^2; at currents higher than 20 microamp/cm^2 intense alkalinity is developed at some isolated areas, whereas the remainder of the specimen is faintly pink.	Small randomly distributed spots of copper are deposited on a cold rolled specimen (Fig. 2*b*). On an annealed specimen, spots of copper appear to be smaller, vary in number from grain to grain, and in many cases follow the grain boundaries (Fig. 2*c*).	Small isolated areas of reddish-brown coloration indicating localized formation of hydrogen peroxide.

resistance of air-formed oxide films on iron (8) and copper (9) is sufficiently low to permit uniform migration of electrons at low current densities. However, the electronic resistance of aluminum oxide (10) is several orders of magnitude higher than that of either ferric oxide or cupric oxide (11). Consequently, this fact might well lead to electrons migrating through thin air-formed aluminum oxide films at local "weak" or thin points, as has been previously supposed by Evans (12).

In order to determine the distribution of effective cathodic areas, tests were carried out on cold-rolled and annealed aluminum (both etched in ½% hydrofluoric acid), iron and magnesium (etched in 2% nital), tin (etched in 5% nital), copper (etched in 1:1 nitric acid), lead (etched in concentrated

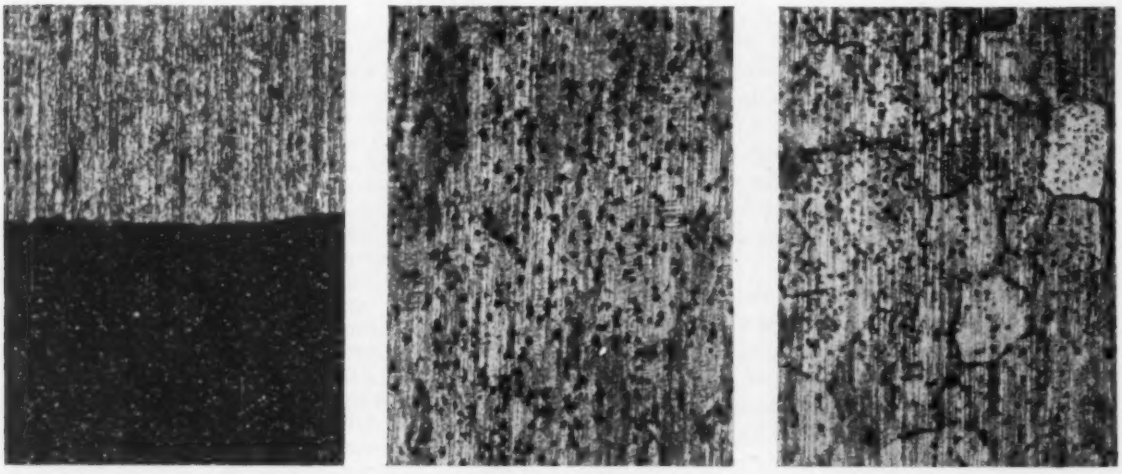

FIG. 2. Distribution of deposited copper on iron, cold rolled aluminum, and annealed aluminum after 2-min cathodic treatment in normal sodium chloride containing 0.1% cupric sulfate. From left to right—(*a*) uniform deposition on iron; (*b*) localized deposition on cold rolled aluminum; (*c*) localized and grain boundary deposition on annealed aluminum. (Magnification 50× before reduction for publication.)

nitric acid), and zinc (etched in 20% chromic acid plus 7.5% sodium sulfate). All specimens had an area of 10 cm² and were stored in dry air for 24 hr after etching in order to permit the formation of air-formed oxide films.

The tests used to investigate the initial distribution of cathodic areas were:

(*A*) Cathodic treatment of the specimen in normal sodium chloride containing one drop of phenolphthalein at a current of 1 microamp/cm² of specimen using a platinum anode. In some experiments the current was varied as shown in Table II. The distribution of the alkali formed during the cathodic reaction indicated the position of the cathodic areas.

(*B*) Cathodic treatment of the specimen for 2 min in normal sodium chloride containing 0.1% of cupric sulfate at a current of 1 microamp/cm² of specimen using a platinum anode. Deposited copper on the specimen also gave an indication of the distribution of the cathodic areas which could be readily photographed.

(*C*) Cathodic treatment in normal sodium chloride containing sodium molybdate at a current of 1 microamp/cm². The distribution of the reddish-brown permolybdate (13) indicates the distribution of hydrogen peroxide on zinc and aluminum cathodes.

In all tests the applied current flowed as soon as the specimen came in contact with the solution.

The results of these tests are shown in Table II. Tests [1] and [2] show that iron, copper, magnesium, zinc, tin, and lead, all carrying air-formed oxide films, act as effective cathodes over most of their surfaces (Fig. 2*a*). However, tests [2] and [3] show that aluminum, when covered with an air-formed oxide film, acts as an efficient cathode only at small isolated points. On cold-rolled aluminum these small cathodes appear to be randomly distributed over the surface of the specimens (Fig. 2*b*). Somewhat similar isolated deposition of copper (from coolant solutions containing cupramines) has been observed on aluminum previously (14). On annealed aluminum the average size of the spots of copper is smaller than on cold-rolled aluminum, but a distinct correlation between the grain boundaries and the copper deposition is apparent (Fig. 2*c*).

These results may be interpreted as meaning that the electronic resistance of the air-formed oxide film on aluminum, unlike those on the other metals studied, is so high that it prevents the migration of electrons to the film/solution interface except at small "weak" points of low electronic resistance. Thus, instead of the cathodic reaction taking place at low current density over most of the surface, as in the case of iron and copper, it takes place at a much higher current density over a small portion of the surface. This will lead to high polarization of the cathodic reaction as shown in Fig. 1. Whereas the "weak" points are randomly distributed on the distorted-cold rolled aluminum, they appear to follow the grain boundaries of annealed aluminum, possibly due to a high degree of lattice misfit in the underlying metal at these areas.

Although additional work remains to be carried out before general conclusions can be advanced, it is felt that these observations throw new light on the high resistance of aluminum to chloride solutions and on the limited sensitivity of the corrosion of this metal to the presence of oxygen.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1956 JOURNAL.

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FUTURE MEETINGS OF
The Electrochemical Society

Pittsburgh, October 9, 10, 11, 12, and 13, 1955

Headquarters at the Hotel William Penn

Sessions will be scheduled on

Batteries, Corrosion, Electrodeposition,
Electro-Organics, and Electrothermics and Metallurgy

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San Francisco, April 29, 30, May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

Sessions will be scheduled on

Electric Insulation, Electronics (including Instrumentation, Luminescence,
Oxide-Cathodes, Phosphor Application, and Semiconductors),
Industrial Electrolytics, Electrothermics and Metallurgy,
and probably Theoretical Electrochemistry

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Cleveland, October 28, 29, 30, 31, and November 1, 1956

Headquarters at the Statler Hotel

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Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

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Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

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Papers are now being solicited for the meeting to be held in San Francisco. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's office, 216 West 102nd Street, New York 25, N. Y., *not later than January 2, 1956* in order to be included in the program. *Indicate on abstract for which division the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.